This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

NS

TIVE

IS

SON

N

By the same Author,

FIVE TABLES IN DIAGRAM SIZE,

FOR FACILITATING THE STUDY OF CHEMISTRY IN THE LECTURE ROOMS AND LABORATORY.

The Set, 5s. 6d.

A COURSE OF

QUALITATIVE CHEMICAL ANALYSIS

BY THE LATE

WM. GEO. VALENTIN, F.C.S.

REVISED AND CORRECTED BY

W. R. HODGKINSON, PHD. (Würzburg),

LATE JODRELL SCHOLAR; FELLOW OF THE INSTITUTE OF CHEMISTRY AND OF THE CHEMICAL, PHYSICAL,
AND GEOLOGICAL SOCIETIES OF LONDON AND OF THE MINERALOGICAL SOCIETY;
SENIOR DEMONSTRATOR AND LECTURER ON CHEMISTRY IN THE SCIENCE SCHOOLS, SOUTH KENSINGTON;
PROFESSOR OF CHEMISTRY AND PHYSICS IN THE ROYAL MILITARY ACADEMY, WOOLWICH;

AND

H. M. CHAPMAN,

ASSISTANT-DEMONSTRATOR OF CHEMISTRY IN THE ROYAL SCHOOL OF MINES AND NORMAL SCHOOL
OF SCIENCE, SOUTH KENSINGTON.

SIXTH EDITION

LONDON
J. & A. CHURCHILL
11, NEW BURLINGTON STREET
1884

19361 e. 17

BODLEIAN LI
6 JAN 85
OXFO

PREFACE

TO THE FOURTH EDITION.

A NEW Edition of my Course of Qualitative Chemical Analysis having become necessary, within two years from the appearance of the last Edition, I have again been guided in the changes which I have made by the experience gained, during the last six years, of its working with Large Laboratory Classes. The Plan of the Book has been left undisturbed. The few alterations and additions which the more recent progress in Chemical Analysis rendered necessary, have been carefully executed; and the original purpose strictly kept in view, for which the Book was written, viz., to serve as an Elementary Text-book for large Laboratory Classes.

The notation employed throughout is that of Dr. Frankland. An experience extending now over a number of years, and gained with students of very varying abilities, has shown me that this notation greatly facilitates the teaching. It complies with the doctrine of Atomicity, which may now be said to have struck firm root in Chemical Literature, and the Chemical Formulæ of Inorganic as well as Organic Bodies, will be found expressed in accordance with this comprehensive and elegant Law.

The study of Chemical Analysis, when properly conducted, introduces the student to a vast number of changes, the verification of which requires, in no mean degree, the cultivation of habits of close observation and exact reasoning; and as a means of mental training, Chemical Analysis cannot fail to acquire a foremost place in the Curriculum of a Liberal Education.

The methods which I selected in this work have stood the test of many years' practice under my own eyes. They are, I believe, well adapted for promoting accurate and expeditious work. Students who apply themselves steadfastly to the study of analysis, usually get through the course in about six months, and have time left to gain some practice also in Quantitative Analysis, during their first year's study. The foundation for this latter branch of Chemistry having been laid by the Qualitative Course, they have, in most cases, only to acquire the necessary manipulatory skill to conduct quantitative operations successfully.

The reactions of the Rare Metals have been treated somewhat more fully than usual in the Appendix. The individuality of the metals as well as the classification which nature itself has traced out for them, have been retained as much as possible. I trust that the additions made in this New Edition will increase the usefulness of the Book, and will gain for it many new friends.

The Analytical Tables are published also in a separate and all but indestructible form, printed on Messrs. De la Rue's parchment paper.

SCIENCE SCHOOLS,
SOUTH KENSINGTON,
September 30*th*, 1876.

PREFACE

TO THE FIFTH EDITION.

THE Fourth Edition of my lamented teacher and predecessor's "Course of Qualitative Analysis" having run out of print, I have, though with considerable diffidence, undertaken the revision of a New Edition.

After having stood such a long and successful test of practical experience in these laboratories, it was not found desirable to make any extensive alteration in the style or plan of the book, for although Chemistry as a science enlarges its bounds and dominion very rapidly, especially Synthetic Chemistry, the road for a beginner must, to a certain stage, at which he should have a clear view of the ground gone over, and the reason of the processes employed, remain the same.

The alterations and additions in the present Edition are such as have been suggested by experience with large classes in Practical Chemistry, since the date of the last one, and it is hoped will add to its utility, and secure it a still wider appreciation.

The Tables for Qualitative Analysis are also published separately, as before, on parchment paper.

SCIENCE SCHOOLS,
SOUTH KENSINGTON,
April, 1880.

PREFACE

TO THE SIXTH EDITION.

2ND REVISED EDITION.

THE present Edition embodies the result of experiences gained by the working of the last Edition. Without altering the general plan of the Work, considerable corrections and additions have been made. The formulæ, or mode of expression of Chemical Compounds, has been slightly simplified, and several modes in common use are employed indifferently throughout the Book, in order to familiarise the Student with them.

Mr. Chapman and myself have together carefully repeated all the tests and experiments detailed in the Work under as many conditions as possible.

I am indebted to Mr. F. Greening for the Map of Spectra in the Appendix.

It is hoped that in its slightly enlarged form the Work will meet with the kindly appreciation accorded to previous Editions.

NORMAL SCHOOL OF SCIENCE,
SOUTH KENSINGTON,
October, 1884.

TABLE OF CONTENTS.

CHAPTER I.

PAGE

Definition of qualitative analysis. Reagents. Chemical operations. Chemical apparatus. Separation into groups. Analytical classification of the metals. Group-reagents and special reagents .. .. .. 1—9

CHAPTER II.

Reactions of the metals of Group V, Potassium, Sodium, Ammonium, Magnesium. Separation of these metals .. .. 10—16

CHAPTER III.

Reactions of the metals of Group IV, Barium, Strontium, Calcium. Separation of these metals .. .. 17—23

CHAPTER IV.

Action of the group-reagents Ammonic Chloride, Ammonia, and Ammonic Sulphide. Reactions of the metals of Group III, Nickel, Cobalt; Separation of Nickel from Cobalt; Manganese; Peroxides of Manganese; Oxidation by Potassic Permanganate; Zinc; Iron; Iron ores, Ferrous and Ferric salts, Ferrates; Chromium, Chromic oxide, Chromic anhydride, Oxidizing action of Chromic anhydride. Chromates. Aluminium. Separation of the metals of Group IIIA. Separation of the metals of Group IIIB .. .. 24—62

CHAPTER V.

Reactions of the metals of Group II. Sulpho-bases, sulpho-acids, sulpho-salts. Subdivisions of Group II. Mercury. Mercurous and mercuric salts. Lead. Bismuth. Copper. Reactions for cupric salts. Precipitation of copper by voltaic action. Cuprous oxide. Cadmium. Separation of the metals of Group IIA. Tin. Stannous and stannic compounds. Antimony. Antimonious and antimonic compounds. Arsenic. Arsenious and arsenic compounds. Reduction of arsenical compounds. Arsenietted and antimonietted hydrogen. Separation of arsenic from antimony. Gold and platinum. Methods for the Separation of arsenic, antimony, and tin .. .. 63—105

CHAPTER VI.

Reactions of the metals of Group I. Silver. Lead, Oxides of Lead. Mercurosum. Separation of the metals of Group I .. .. .. 106—116

PAGE

Non metals—Carbon, Silicon, Boron, Oxygen, Sulphur, Nitrogen, Phosphorus, Chlorine, Fluorine, Bromine, Iodine .. .. .. 116—122
Alcohol, Ether, Benzene, Bisulphide of Carbon .. .. .. 122—125

CHAPTER VII.

Reactions of inorganic acids. Carbonic anhydride. Sulphuric acid. Sulphurous acid; Reducing and oxidizing action of sulphurous acid. Hyposulphurous acid. Hydrosulphuric acid. Sulphides. Nitric acid. Nitrous acid. Hydrochloric acid. Chloric acid. Hypochlorous acid. Hydrobromic acid. Preparation of bromine and hydrobromic acid. Bromic acid. Hydriodic acid. Iodic acid. Hydrofluoric acid. Preparation of hydrofluoric acid. Preparation of hydrofluosilicic acid. Hydrofluosilicic acid. Phosphoric acid. Pyro- and metaphosphoric acids. Phosphorous and hypophosphorous acids. Silicic acid. Analysis of silicates. Boric acid. Hydrofluoboric acid. Hydrocyanic acid. Single cyanides. Double cyanides. Preparation of hydrocyanic acid. Hydroferrocyanic acid. Hydroferricyanic acid. Ferricyanides. Hydrocobalticyanic acid. Cyanic acid. Sulphocyanic acid .. .. 125—182

CHAPTER VIII.

Organic acids. Compound organic radicals. Formic acid. Series of fatty acids. Acetic acids. Stearic acid. Benzoic acid. Succinic acid. Oxalic acid. Preparation of carbonic oxide. Tartaric acid. Citric acid .. .. 182—194

Practical exercises, comprising simple salts and compound bodies 195
Tables for the qualitative analysis of simple and compound substances, both in the dry and wet way .. .. 197—239

APPENDICES.

I. Reactions of the Rare Metals. Separation into Groups. Reactions of the metals of the Alkali Group: Cæsium, Rubidium, Lithium. Reactions of the metals of Group III: Glucinum, Zirconium, Thorium, Yttrium, Erbium, Scandium, Ytterbium, Terbium, Cerium, Lanthanum, Didymium, Titanium, Tantalum, Niobium, Uranium, Thallium, Indium, Gallium, and Vanadium. Reactions of the metals of Group II: Palladium, Rhodium, Osmium, Ruthenium, Iridium, Davyium, Molybdenum, Tellurium, and Selenium. Reactions of the metals of Group I: Tungsten or Wolfram. Newland's Table of Elements .. .. 240—284
II. Reagents. Solvents. Acids. Bases and metals. Salts. Metals and oxides. Vegetable colouring matters .. .. .. 285—296
III. Table showing the solubility of salts in water and in acids .. 297—301
IV. Schemes for recording analytical results .. .. .. 302—305
V. Chart of Spectra 306

A COURSE

OF

QUALITATIVE CHEMICAL ANALYSIS.

CHAPTER I.

DEFINITION OF QUALITATIVE ANALYSIS.—REAGENTS.—CHEMICAL OPERATIONS.—GROUP-REAGENTS AND SPECIAL REAGENTS.

THE practical object of chemical analysis is to discover the presence or absence of some one or more of the chemical elements in any given and unknown substance. With this view experiments are performed on the substance—in fact questions are put to it—and from the result of these experiments, or the answers to these questions, the nature of the substance or substances is deduced; the answers or results of the experiments which the chemical elements give under the same experimental conditions being known.

The elements of most widely differing character have still many points of resemblance in their behaviour towards other elements or groups of elements, and in many cases groups of elements are so similar in their general behaviour under the same circumstances that they may be said to have a family resemblance, or form a closely connected group. Consequently in applying chemical tests, as in mathematical, a regular order of procedure is necessary, so as not to confound the indications or answers of an individual element with those of a group or the reverse.

Starting from the fixed properties of the elements, and noting their general and particular resemblance and points of dissimilarity, the methods of distinguishing and separating the elements or groups of elements in a complex substance will be found, as an exercise of the reasoning faculties of the student, little inferior to mathematical methods.

From this it follows that the properties of the elements themselves must be first studied.

The necessity of " exactness " in the performance of all operations cannot be too distinctly impressed on the chemical student. Chemical actions only take place on the actual contact of the substances under experiment. There is no such thing as " nearly,"

66

either a chemical action takes place or it does not; very often, however, an action commences but slowly, and may take some time before being completed.

Reagents are employed as the means of producing chemical changes. By reagents are meant bodies—either elementary or compound—which are capable of *acting* upon and revealing to us, by bringing about changes, the nature of the substances under examination. They are usually divided, without any strict line of demarcation, into two classes, viz., *general* and *special reagents.* General reagents are those which separate a number of substances —groups in fact—at one operation; and special reagents those which are used to a limited extent only, and for the detection of *individual* substances.

In a laboratory the general reagents are most conveniently arranged over the working table within reach of each operator; whilst the special reagents intended for the use of a number of chemical students, are usually placed in a freely accessible part of the laboratory.

A list of reagents, as well as directions for their preparation, will be found in an Appendix. Chemical students who have not the advantage of working in a well-appointed laboratory, should devote much attention and care to the preparation of the reagents.

Chemical Operations. — **A reagent is added** to a solution of an unknown body either by pouring it directly from the bottle or by running it from a pipette, as shown in Fig. 1, with the view of producing a **precipitate,** *i.e.*, of converting the body from the soluble to the insoluble state. The reaction which takes place is mostly *a change by double decomposition.* Sometimes a precipitation is produced by voltaic action, sometimes merely by the substitution of one solvent for another. One or more bodies may be precipitated by one and the same reagent. As most precipitates are heavier than the liquid in which they are suspended, they fall to the bottom with more or less rapidity; and the supernatant liquid may often be poured off or **decanted,** without much disturbing the precipitate. This mode of separating fluids from precipitates is by far the most expeditious, and should be resorted to whenever it is applicable. The precipitate

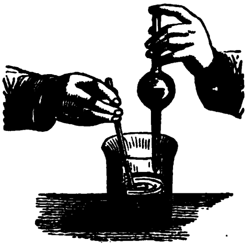


FIG. 1.

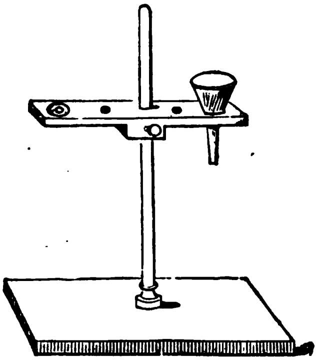


FIG. 2.

may be washed in the vessel itself by treatment with hot water and repeated decantation.

When a large quantity of a fluid has to be removed from a precipitate, it is best to **siphon** off the supernatant fluid. The precipitate may be washed with water, and the wash-water siphoned off repeatedly.

Small quantities of a precipitate which do not subside readily are more quickly separated by **filtration.** For this purpose **funnels** are used, mostly of glass, conical in shape, and inclined at an angle of 60°. They may be conveniently supported on a wooden stand, Fig. 2, or an iron or brass **filtering stand** as seen in Fig. 3. The **filtering paper** should be porous and unsized, and cut in the form of a round sheet, which by being folded twice in the shape of a quadrant, forms, on opening up, a paper cone, at an angle of 60°. The **filter** should exactly fit the funnel, without reaching quite to the rim, and should be moistened in the funnel with distilled water before any liquid is poured through it. As most kinds of filtering paper contain traces of iron, lime, silica, etc.,—with the exception of the so-called Swedish filtering paper, which contains scarcely perceptible traces of mineral substances,—acid liquids frequently dissolve out traces of these bodies. In all accurate analyses the filtering paper should, on this account, be washed first with dilute hydrochloric or nitric acid, and then with hot water, before being used; or else Swedish filter paper only should be employed.

Most precipitates retain with great pertinacity traces of the fluid in which they were suspended, and it is therefore of the utmost importance to thoroughly wash them in order to obtain accurate results. For this purpose a **wash-bottle** (Fig. 3) is employed, whereby a fine jet of hot or cold distilled water can be directed on to the filter in such a manner as to loosen and detach the precipitate from the paper. *The liquid should at no time quite fill the filter, as some precipitates have a tendency to creep up and to get between the paper and the glass, and are carried into the* **filtrate.** *This would entail repeated filtration.* The washing of a precipitate on the filter is effected most rapidly by allowing the wash-water to run off entirely each time before adding fresh quantities of distilled water. By repeating this four or five times, most precipitates will be found sufficiently washed for qualitative purposes.

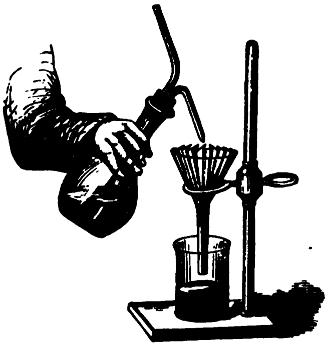


FIG. 3.

The student should guard himself against using *too large* a quantity of the substance which he wishes to examine. Bulky or voluminous precipitates entail much washing, an operation which is most tedious and yet indispensable.

Test-tubes are the vessels used for the operations of precipitation and separation in qualitative analysis, especially as there is generally no need for collecting the wash-water or adding it to the main filtrate. These tubes are conveniently placed in a **test-tube stand** (Fig. 4). After being well cleansed by the aid of a test-tube brush, and rinsed out with distilled water, they should be set aside to drain in a basket.

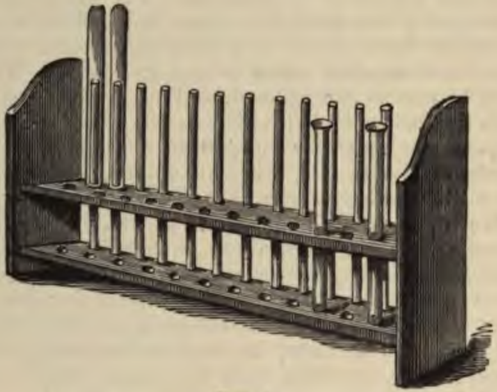


Fig. 4.

Beakers are sometimes employed if an analysis involves the separation of a small quantity of one substance from a large amount of another, and when, of necessity, large quantities of the substance must be operated upon.

Porcelain dishes are employed for the purpose of concentration, or evaporation and ignition. They can be heated either by means of a **spirit lamp** (Fig. 5), or by means of a **Bunsen gas lamp**, provided with a rose top. Sometimes a sheet of iron wire gauze or a sand-bath is interposed between the porcelain vessel and the gas flame, and is supported on a retort ring, or tripod stand. Illustrations of convenient tripod supports for porcelain and glass vessels, which prevent at the same time the flame from being blown about, have been given in the "Introduction to Inorganic Chemistry."

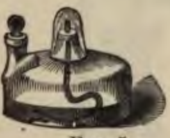


Fig. 5.

If solid substances have to be examined, they should always be **powdered** in a **mortar**—an agate mortar should be employed for hard substances, such as minerals—before being dissolved in water, acids, &c.

Reactions involving the use of valuable reagents—such as salts of gold, platinum, silver—should be performed on **watch-glasses**, with small quantities of the substance only.

For the **ignition** of precipitates, porcelain crucibles, or small porcelain dishes are used.

A knowledge of qualitative analysis enables us—

1. *To recognise with speed and certainty the presence of various elementary and compound bodies.*
2. *To effect their separation from each other.*

In order to accomplish this it is necessary to study more particularly those chemical reactions—both in the dry and in the wet way—that is to say, by the action of heat under different circumstances and by the action of reagents on the substance when in solution in water or other liquid—which are essential; and also endeavour, at the same time, to get as complete a view as possible of other chemical changes which serve the purposes of qualitative analysis, and which on this and other grounds possess considerable interest.

It is for many reasons desirable to confine the laboratory course at first to the study of the more important elements and their compounds; the so-called rarer elements and their compounds are treated of in a separate Appendix.

The term rare elements is only one of distinction, some of the substances being very widely distributed in nature, but not utilised to any important extent as yet.

There are certain reagents which effect the separation of a number of bodies contained in a common solution, leaving all the others in solution. Such general reagents are then called *group-reagents.*

Dissolve in water small quantities of

Argentic nitrate.*
Cupric nitrate.
Cobaltic ,,
Baric ,,
Potassic ,,

To the solution add—

Hydrochloric acid, a *white curdy* precipitate is obtained, which consists of **argentic chloride**, AgCl; filter. To the filtrate add—

Sulphuretted hydrogen, a *black* precipitate is obtained consisting of **cupric sulphide**, CuS; filter again, and to the filtrate add—

$\left.\begin{array}{l}\text{Ammonic chloride,}\\ \text{Ammonia and}\\ \text{Ammonic sulphide}\end{array}\right\}$ A *black* precipitate comes down consisting of **cobaltous sulphide**, CoS; filter, and to the filter add—

Ammonic carbonate, a white precipitate is obtained, consisting of **baric carbonate**, $BaCO_3$; filter, evaporate the filtrate and ignite to drive off the ammonic salts. A white saline residue is left, containing the **potassic salt**.

What were the chemical changes that took place?

The changes were evidently produced *by the mutual exchange of elements in two bodies* (changes by *double decomposition*): *i.e.*, the hydrochloric acid added in Group I to the solution of the metallic nitrates, exchanged its hydrogen for the silver of the argentic nitrate; and the sulphuretted hydrogen exchanged its hydrogen for the metal copper, leaving nitric acid and cupric sulphide, etc.

---

* Solutions of salts of the different metals containing five milligrammes of the metal in a cubic centimetre are conveniently prepared and kept for use.

The reactions will be readily expressed by equations, thus:—

$AgNO_3$	+	HCl	=	$AgCl$	+	HNO_3.
Argentic nitrate.				Argentic chloride.		
$Cu(NO_3)_2$	+	SH_2	=	CuS*	+	$2HNO_3$.
Cupric nitrate.				Cupric sulphide.		
$Co(NO_3)_2$	+	SAm_2	=	CoS	+	$2NH_4NO_3$.
Cobaltous nitrate.				Cobaltous sulphide.		
$Ba(NO_3)_2$	+	Am_2CO_3	=	$BaCO_3$	+	$2NH_4NO_3$.
Baric nitrate.				Baric carbonate.		

Silver, copper, cobalt, and potassium are, however, not the only metals which might have been separated by these same reagents.

The table on the next following page exhibits the five groups into which all metallic bodies classify themselves on the addition of the several group-reagents.

Thus far *group*-reagents assist in the separation of bodies, but when, as in Group IV, the white precipitate produced by the group-reagent, ammonium carbonate, leaves still a doubt whether a barium, strontium, or calcium compound was present in the solution, further experiments must evidently be made with a view of completely identifying the substance under examination. This the student will only be able to do by making himself first practically familiar with the different changes or reactions which the members of the various groups of metals can be made to undergo: and after understanding the use of the group-reagents, he should direct his attention to the special reactions *which distinguish and separate one metal from another, or from several others.* THIS MAY FREQUENTLY BE DONE IN MORE THAN ONE WAY; ONE REACTION, HOWEVER, SOMETIMES DESERVES THE PREFERENCE OVER OTHERS, ON ACCOUNT OF THE GREATER EXACTNESS WHICH DISTINGUISHES IT, OR ON ACCOUNT OF INCREASED FACILITY OF EXECUTION, OR OF BOTH.

Certain reactions, lastly, will have to be studied, which are not directly available for the separation of the members of a group from each other, but to which considerable interest is attached as being illustrative of some valuable property or other of the metals.

The tabular form, which is, no doubt, the most compact and

---

* It is immaterial whether written SCu or CuS, since both sulphur and copper are dyad elements.

ANALYTICAL CLASSIFICATION OF THE METALS,

WITH THEIR RESPECTIVE GROUP-REAGENTS.

GROUP I. Hydrochloric Acid.	GROUP II. Sulphuretted hydrogen, in acid solutions.	GROUP III. Ammonic Chloride, Ammonia, and Ammonic Sulphide.	GROUP IV. Ammonic Chloride, Ammonia, and Ammonic Carbonate.	GROUP V. (No group-reagent.)
Lead.... as $PbCl_2$.*	Mercury....... as HgS, *black.*	(1.) **Hydrates.**	Barium as $BaCO_3$.	**In solution:**
Silver... „ $AgCl$.	Lead.......... „ PbS,‡ „	Aluminium.. as $Al_2(HO)_6$.	Strontium „ $SrCO_3$.	Magnesium.
Mercury „ Hg_2Cl_2.†	Bismuth....... „ Bi_2S_3, „	Chromium .. „ $Cr_2(HO)_6$, *green.*	Calcium „ $CaCO_3$.	Potassium.
	Copper........ „ CuS, „	(2.) **Sulphides.**		Sodium.
	Cadmium...... „ CdS, *yellow.*			Ammonium.
	Tin (Stannosum) „ SnS, *black.*	Iron........ „ FeS, *black.*		
	„ (Stannicum) „ SnS_2, *yellow.*	Zinc........ „ ZnS, *white.*		
	Antimony..... „ Sb_2S_3, *orange.*	Manganese.. „ MnS, *buff.*		
	Arsenic........ „ As_2S_3, *yellow.*	Nickel...... „ NiS, *black.*		
	Gold.......... „ Au_2S_3, *black.*	Cobalt...... „ CoS, „		
	Platinum...... „ PtS_2, „	(3.) **Certain Salts,**		
		such as alkaline earthy phosphates, &c., &c.		

---

* When no colour is stated, the precipitate is *white.* There are degrees of whiteness, however, depending on the physical condition, density, crystalline form, &c., of the precipitate.

† Precipitated as mercurous chloride from mercurous salts.

‡ Lead being somewhat soluble in cold water in the form of plumbic chloride, $PbCl_2$, it is found both in the first and second group.

summary mode of arranging chemical reactions, will often be adopted for embodying such reliable and expeditious methods of separation as have stood the test of experience in the laboratory. The directions given will be concise and divested of all explanatory matter. On no account should a student use any tabular directions, however, without first having made himself practically acquainted with the details of the reactions; and to counteract any pernicious influence which the use of tables might have, the student should learn to draw up tables for the several other processes of separation which are frequently possible.

A deviation from the natural course of studying the reactions of the metals by beginning with Group I, and so on, will be justified on the ground of greater simplicity, and on account of the far greater importance which is attached to the metals of Group V, especially the alkali metals. Experience has shown that students have less difficulty in mastering the reactions by reversing the order of the groups, beginning with the study of the alkali and alkaline-earthy metals; and that a thorough knowledge of the metals of these groups is of material assistance in understanding the qualitative changes to which the metals proper are subjected.

Chemical nomenclature has, of necessity, undergone changes of form from time to time as one theory or another has been more or less fully borne out by facts. For that reason several methods of writing the chemical formulæ of bodies are employed in this work for the purpose of making the student accustomed to the different forms in use. It must not, however, be supposed that in all cases any one kind of formula is more correct than another in representing the *structure* of compounds. In organic chemistry it is very essential to arrive at the *structure* of the compound which is sought to be expressed by a constitutional formula. In qualitative analysis this is not so much the case. It is essential to know only the composition of the substances dealt with. A constitutional formula is, however, always more useful than a purely empirical one; but in the case of many mineral substances this is very difficult if not impossible at present to arrive at with any certainty; as in organic bodies and in other cases several formulæ express different methods of construction of the same compound. For instance, in the case of sulphuric acid, the oxide of sulphur, SO_3, combines directly with water, OH_2, forming the acid; therefore, the composition might be written SO_3OH_2: but when SO_2, the lower oxide of sulphur, comes in contact with hydroxyl, $(HO)_2$ H_2O_2, sulphuric acid is also formed and might be written as $_2(HO)_2$; also when SO_2 comes in contact with PbO_2 there is a sulphate directly produced, PbO,SO_2; and again when a metal s upon the acid, hydrogen is evolved, the action of which may represented as $H_2SO_4 + M_2 = M_2SO_4 + H_2$; and the decomsition and recomposition of sulphuric acid or sulphates under e action of the galvanic current also seems to support this view its constitution.

However, these questions cannot be discussed in this place.

It should be borne in mind that when a metal has entered into combination with another substance it has lost some of its individuality. It is not the same in combination as when alone. To some extent the new compound acts as an independent individual, its characters being influenced to a greater or less degree by those of its constituent elements. One of these elements in a compound usually imparts its character in a dominant degree, as in the case of the metallic compounds termed salts, from which we get the reactions of the metals in combination.

The student should exercise himself in writing the formulæ of substances in as many forms as possible, and in each case study the synthetical processes indicated by or which have led to the formula.

The combining values, or the atomicities of the elements, are indicated in symbolic notation by the use of dashes and Roman numerals placed above the symbols of the elements, thus:—H', Zn'', Au''', C^{iv}, N^{v}, S^{vi}, but this value is possibly variable.

These combining values or atomicity marks do not at all indicate the intensity of chemical attraction or energy of union, but merely the extent or quantity of attraction of one element for another expressed in terms of hydrogen as the unit.

CHAPTER II.

REACTIONS OF THE METALS OF GROUP V.

THIS group comprises the metals POTASSIUM, SODIUM, AMMONIUM, and MAGNESIUM, which are not precipitated by any group-reagent.

1. **POTASSIUM**, K. Atomic weight, 39·1. Specific gravity, 0·87. Melting point, 62·5° C. Boiling point, 719—731° C.—Is found in combination in large amount only in a few minerals, of which *nitre* or *saltpetre* is the most important. It is present in larger or smaller quantities in a few silicates and sulphates, such as *felspar*, *alumstone*, in the ashes of plants (*crude potashes*), and in the form of chlorine in saline deposits (at Stassfurth, in Prussia, and elsewhere).

The metal has a brilliant silver-white lustre in a freshly cut surface, which immediately tarnishes on contact with air, becoming covered with oxide. It decomposes water when brought in contact with it, the heat produced being sufficient to inflame the liberated hydrogen. The metal is so soft that it may be squeezed easily by the fingers. It is kept under rock oil or paraffin, to prevent oxidation.

REACTIONS IN THE DRY WAY.

Most potassium compounds, when heated in small quantities on a thin platinum wire in the inner flame of the blowpipe, undergo dissociation, the vapour of the metal imparting a **violet colour** to the outer flame. When examined with the aid of a spectroscope,*

---

* When elements in the gaseous condition, or vaporised by strong ignition, are analysed by means of the spectroscope, they may be distinguished from each other by the respective spectra which they give. The intensity of the spectra of metallic elements is so much greater than that of the non-metals, that the latter are only rarely seen. The heat which can be produced by a good Bunsen gas burner is not strong enough to volatilize all elements, or to heat their vapour highly enough. Most heavy metals can only be volatilized by means of an electric spark, making use of an induction coil, by placing the galvanically precipitated metals between the electrodes. In order to analyse the ordinary gases spectroscopically, the spark is passed through the gases confined in Geissler tubes.

It is usual to employ the spectroscope only for the examination of those metals, or metallic compounds, which can be volatilized by means of the gas flame from a good Bunsen burner, such as the alkali metals, sodium, potassium, rubidium, cæsium, lithium; the alkaline earthy metals, barium, strontium, calcium; and the heavy metals, thallium and indium. The compounds most suitable are the chlorides, nitrates, chlorates, perchlorates, and carbonates of these metals. A small portion is placed on the loop of a thin platinum wire, introduced into the non-luminous portion of the flame, and the spectrum examined. The different elements are distinguishable by their respective colours, as well as by the position which their lines occupy in the continuous solar the potassium spectrum is found to consist mainly of two lines, a comparatively strong line, $K\alpha$,\* in the RED, and a faint line, $K\beta$,\* in the BLUE.

This applies more particularly to potassic salts which are volatile without decomposition at a very strong heat (such as potassic chloride, bromide, iodide, and cyanide) or which are decomposed by heat; but not to non-volatile potassic salts, such as phosphates, silicates, or borates, which give scarcely any flame reaction till they are moistened with HCl, or, if HCl be without action, heated together with pure calcic sulphate. The presence of sodium compounds gives rise to an intense *golden-yellow* flame, and conceals the potassium reaction; but when seen through a blue glass, or indigo-prism, the yellow or sodium flame is entirely cut off, and the potassium flame becomes distinctly visible, and is then of a *rich reddish-violet* colour.

REACTIONS IN THE WET WAY.

A SOLUTION OF POTASSIC CHLORIDE, KCl, is used.

$PtCl_4$ (**platinic chloride**) precipitates from potassic solutions which are not too dilute, a *yellow crystalline* precipitate of **potassic platinic chloride,** $2KCl,PtCl_4$, insoluble† in strong alcohol, or better still in alcohol and ether, as well as in acids.

$\left\{\begin{array}{l}COHO\\CHHO\\CHHO\\COHO\end{array}\right.$ (**tartaric acid**) precipitates *white crystalline* **hydric potassic tartrate,** $\left\{\begin{array}{l}COKO\\CHHO\\CHHO\\COHO\end{array}\right.$ from neutral and sufficiently concentrated solutions. The precipitate settles rapidly, especially on shaking or stirring.

$2HF,SiF_4$ (**hydrofluosilicic acid**) gives a *white gelatinous* precipitate of **potassic silicofluoride,** $2KF,SiF_4$; difficultly soluble in water (833 parts at 17·5° C.); insoluble in alcohol.

Potassic salts are for the most part soluble in water, hence so few visible reactions; the hydrate and carbonate constitute two important reagents, on account of the great affinity which the powerful base potassium possesses for the acids with which the metals of other groups may be combined.

---

spectrum. The lines are not all of the same intensity, and therefore not equally available.

It is only by employing large quantities of pure substances, and heating them very intensely, that many of the less prominent lines can be observed. The accuracy of the reactions is, however, so great that we can discover in this manner the merest traces of these elements, and are enabled to disentangle mixtures thereof, without actual separation. Spectroscopic analysis constitutes in fact a most valuable auxiliary to chemical analysis.

* *Principal* spectral lines of elements are generally designated by a letter for ordinary reference purposes.

† The degree of solubility of a precipitate in different media can only be ascertained by laborious *quantitative* experiments. The student will therefore be expected to verify only those statements respecting the solubility of the precipitates which require no quantitative knowledge.

2. **SODIUM,** Na. Atomic weight, 23. Specific gravity = 0·974. Melting point, 96° C.—This metal resembles potassium in appearance, but is a little harder, and does not oxidise so rapidly in air, nor is its action on water so energetic as that of the latter metal. It occurs in nature in vast masses, as *rock salt*, NaCl; as CARBONATE, in *native soda*, $Na_2CO_3,10OH_2$, and in *trona*, $Na_2CO_3,2COHONaO,3OH_2$; as NITRATE, in *cubic nitre*, or *Chili saltpetre*, $NaNO_3$; as SULPHATE or *glauber salt*, $Na_2SO_4,10OH_2$; as *biborate*, $Na_2B_4O_7,10OH_2$; as *glauberite*, $S_2O_4(NaO)_2CaO_2$; and as *cryolite*, $6NaF,Al_2F_6$; and in many SILICATES, of which *albite* may be taken as the representative. All natural sodium compounds, with the exception of the last two minerals, are soluble in water.

REACTIONS IN THE DRY WAY.

The intense **golden-yellow** colour which sodium compounds impart to the outer blowpipe flame is almost exclusively relied upon for the detection of the metal. Its spectrum consists of one bright double line, coinciding with the D line of the solar spectrum, and several green lines seldom seen. Some sodic salts are readily recognised by their characteristic taste, especially rock salt and cubic nitre.

REACTIONS IN THE WET WAY.

A SOLUTION OF SODIC CHLORIDE, NaCl, is employed.

Sodic salts are even more freely soluble than potassic salts, and platinic chloride or tartaric acid give no precipitates. Hydrofluosilicic acid gives a gelatinous precipitate from concentrated (aqueous) solutions only; the precipitate is insoluble in alcohol.

Sodic hydrate and sodic carbonate act in many respects like potassic hydrate and carbonate.*

3. **AMMONIUM,** Am = NH_4. Atomic weight, 18. Hypothetical metal or "compound radicle" in combination.

REACTIONS IN THE DRY WAY.

Ammonic salts, when heated in a test-tube, **volatilize**, either entirely or partially. Salts with fixed acids, such as phosphoric acid, lose ammonia, NH_3. Salts of ammonium with volatile acids can be volatilized, either with decomposition, such as the nitrate, nitrite, sulphate, the latter with formation of mixed vapour of nitrogen, water, ammonia, and sulphurous anhydride; with partial dissociation only, such as the chloride, bromide, iodide: the latter salts condense again, for the most part unchanged; they *sublime*, and are found in the upper part of the test-tube.

---

* The student who has not the advantage of attending a course of lectures on chemistry should make himself familiar, by reading a good Manual of Chemistry, with the properties of the various salts of potassium and sodium, also with the interesting processes of manufacturing sodic carbonate from the chloride; sodic silicate (*water-glass*); potassic chlorate, etc., etc.

REACTIONS IN THE WET WAY.

A SOLUTION OF AMMONIC CHLORIDE, AmCl, is employed.

$PtCl_4$ produces a *heavy yellow* precipitate of **ammonic platinic chloride**, $2AmCl,PtCl_4$. The precipitate is soluble in much water (hence there appears no precipitate from dilute ammonic solutions), but insoluble in alcohol and ether. Ammonic platinic chloride leaves on ignition only spongy platinum. (DISTINCTION FROM POTASSIC PLATINIC CHLORIDE, which leaves spongy platinum and potassic chloride, $Pt + 2KCl$.)

Tartaric acid produces from a concentrated solution of ammonic chloride a *white crystalline* precipitate of **hydric ammonic tartrate**, resembling the potassium precipitate in its properties. The two precipitates are readily distinguished on ignition. Hydric potassic tartrate leaves a carbonaceous residue, which is strongly alkaline, and the potassic carbonate which it contains dissolves in water. The other leaves merely a residue of carbon, devoid of any alkaline reaction.

Ammonic salts are decomposed, with evolution of ammonia gas, when heated with a hydrate of an alkali (KHO, NaHO, or alkaline earthy metal, $Ba(HO)_2$, $Ca(HO)_2$, thus:—

$$2AmCl + Ca(HO)_2 = 2NH_3 + CaCl_2 + 2OH_2.$$

Neutral or normal salts of certain polybasic acids, *e.g.*, well dried alkaline chromates, borates, phosphates, etc., readily decompose ammonic salts, especially when heated with evolution of ammonia gas, and formation of acid salts, thus:—

$$2K_2CrO_4 + 2AmCl = \left\{\begin{array}{l} CrO_2KO \\ O \\ CrO_2KO \end{array}\right. + 2NH_3 + 2KCl + OH_2.$$

This reaction distinguishes, therefore, between *normal* and *acid* salts of polybasic acids.

Ammonia gas is readily recognised, 1st, by *its pungent odour;* 2nd, by *its turning red litmus paper*, moistened with a drop of distilled water, *blue;* 3rd, by *its combining with the vapour of volatile acids* (such as *dilute* hydrochloric acid) to form white fumes (AmCl).

Nessler's test* for *traces* of ammonia.—If a potash solution of potassic mercuric iodide, $2KI,HgI_2$, be added to a fluid containing mere traces of ammonia or of an ammonic salt, a *brown* precipitate of dimercurammonic iodide, or a *yellow to brown coloration* is produced, according to the quantity of the ammonium compound present—

$$2(2KI,HgI_2) + 3KHO + NH_4HO = \underset{\text{Brown pp.}}{NHg''_2I,OH_2} + 7KI + 3OH_2.$$

---

* For the preparation of the Nessler's solution, see Appendix.

Ammonic hydrate and carbonate, as well as various other ammonium compounds, *e.g.*, ammonic chloride, ammonic sulphide, are among the most useful reagents which the chemist possesses.

QUESTIONS AND EXERCISES.

1. How are potassium compounds recognised in the wet way?
2. How can potassium and sodium compounds be distinguished before the blowpipe flame?
3. State how you would ascertain whether the yellow precipitate produced by platinic chloride indicates the presence of a salt of ammonium or potassium.
4. How can hydric potassic tartrate be distinguished from hydric ammonic tartrate?
5. Which sodic salts are found native?
6. How is spongy platinum prepared?
7. How would you test for mere traces of ammonia?
8. How much spongy platinum is obtained from 2·345 grms. of ammonic platinic chloride?
9. How much dry ammonia gas by volume (litres) and weight can be obtained by distillation with calcic hydrate from 5 grms. of ammonic chloride?
10. How would you examine a mixture containing ammonic chloride and potassic chloride?
11. A mixture of 1·5 grm. of sodic and ammonic chloride lost on ignition ·234 grm.; what is the percentage of ammonic and sodic chloride present in the mixture?
12. Calculate the percentage composition of borax.

4. **MAGNESIUM**, Mg″. Atomic weight, 24. Specific gravity = 1·75. Melting point, 750° C. Boils at about 1100° C.—This metal is silver white, malleable and ductile, does not oxidise in dry air, but is readily acted upon by acids, and also decomposes water when boiled with it. It occurs in nature as OXIDE, in the mineral *periclase*, MgO; as HYDRATE in *brucite*, $Mg(HO)_2$; as CARBONATE in *magnesite*, $MgCO_3$, and in *hydromagnesite*,

$$C_3O(HO)_2MgO_2,3OH_2;$$

as DOUBLE CARBONATE in *dolomite*, $\begin{matrix}CO\\CO\end{matrix}CaO_2MgO_2$, and *mesitine spar*, $\begin{matrix}CO\\CO\end{matrix}MgO_2FeO_2$; as SULPHATE in *kieserite*, $SO(HO)_2MgO_2$ (from Stassfurth salt), and in *epsomite*, $SO(HO)_2MgO_2,6OH_2$; as SILICATE in *peridote*, $Si(MgO_2)_2$, *enstatite*, $SiOMgO_2$, *steatite*, $Si_4O_5(MgO_2)_3$, *talc*, $Si_5O_6(MgO_2)_4$, *serpentine*, $\begin{matrix}SiHOMgO_2\\SiHOMgO_2\end{matrix}MgO_2$, and in *diopside*, $\begin{matrix}SiO\\SiO\end{matrix}CaO_2MgO_2$; and as BORATE in *boracite*, $B_8O_9(MgO_2)_3$.

REACTIONS IN THE DRY WAY.

Magnesic salts, as such, impart *no* colour to a non-luminous gas-flame. The most characteristic reaction for magnesia, in the dry way, is the *pale rose* colour which this alkaline earth acquires on moistening with cobaltous nitrate, and then igniting it once more strongly on charcoal.

This colour can, however, only be relied on when no other metallic oxides are present; and as magnesium salts do not colour the outer blowpipe flame, recourse must almost invariably be had to the reactions in the wet way. Ignition of the sulphate on charcoal in the reducing flame yields the sulphide, MgS. Prolonged ignition of the carbonate yields caustic magnesia, which is almost insoluble in water.

REACTIONS IN THE WET WAY.

For this purpose a SOLUTION OF MAGNESIC CHLORIDE, $MgCl_2$, or MAGNESIC SULPHATE, $MgSO_4 = (SO_2(O_2Mg))$, is employed.

Magnesia is not precipitated by ammonia in the presence of ammonic chloride, because it forms a *soluble double chloride*, $2AmCl,MgCl_2$. In the absence of ammonic chloride, part of the magnesia is precipitated as hydrate, $Mg(HO)_2$, thus—

$$2MgCl_2 + 2AmHO = Mg(HO)_2 + \underset{\text{Soluble double chloride.}}{2AmCl,MgCl_2}.$$

In the presence of a sufficient amount of ammonic chloride, the magnesic hydrate is at once decomposed into magnesic chloride $Mg(HO)_2 + 2AmCl = MgCl_2 + 2AmHO$, and no precipitation takes place, nor is the double chloride precipitated by ammonic, sodic, or potassic carbonate. Hence magnesium cannot be precipitated in Groups III and IV, *provided a sufficient amount of ammonic chloride be present, and the solution be kept sufficiently dilute.*

Potassic, sodic, calcic, and baric hydrate precipitate magnesia almost completely as *white* **magnesic hydrate**, nearly insoluble in cold and hot water. Ammonic chloride, as well as other ammonic salts, dissolve it readily, or, if originally present in sufficient quantities, prevent its formation.

Ammonic oxalate gives, after some time, from moderately dilute solutions of magnesic salts, a *white crystalline* precipitate of a double oxalate of magnesia and ammonia; not so, however, in the presence of excess of ammonic chloride.

$HNa_2PO_4 = POHO(NaO)_2$ (**hydric disodic phosphate**), or better still, a solution of microcosmic salt, precipitates **hydric magnesic phosphate**, $MgHPO_4 = PO_2HOMgO$.

The precipitation is complete in the presence of ammonic chloride and ammonia. $AmMgPO_4$, **ammonic magnesic phosphate**, falls as a *white crystalline* precipitate. The separation from a dilute solution of a magnesic salt is promoted by gentle heat, and by stirring with a glass rod. The precipitate is but slightly soluble in water and ammonic salts. In water containing ammonia it is practically insoluble. Dilute mineral acids dissolve it, as well as acetic acid. From very dilute solutions the precipitate separates only on standing for about 24 hours in a warm place.

On heating magnesic chloride with precipitated mercuric oxide, **the chloride is converted into oxide**, mercuric chloride being volatilized. This experiment must be conducted in a closet which is provided with a good indraught of air, and is in connection with a chimney flue.

Methods for the recognition of Mg, K, Na, and Am will readily suggest themselves, if the student bears in mind—

1st. *The volatility of ammonic salts* (phosphates and borates excepted).

2nd. *The insolubility of* $Mg(HO)_2$ *in water.*

3rd. *The insolubility of* $2KCl,PtCl_4$ *in alcohol.*.

4th. *The intense yellow coloration* which sodium imparts to the blowpipe flame.

A solution containing salts of Mg, K, Na, and Am may be examined as follows:—

1st. Heat a portion with NaHO; ammonia gas is given off, which is recognised by its pungent odour, etc.—**presence of** Am.

2nd. To a second portion add ammonium chloride, ammonia, and sodic phosphate; a *white crystalline* precipitate indicates the **presence of** Mg.

3rd. Evaporate a third portion to dryness and ignite strongly. Extract with hot water (without filtering off any magnesic oxychloride (Mg_2OCl_2), which may have been formed), and add sufficient $Ba(HO)_2$ till the whole of the magnesia is precipitated as $Mg(HO)_2$; filter. To the filtrate add Am_2CO_3 as long as a precipitate is produced, and filter again. Evaporate the filtrate to dryness, and ignite strongly to expel ammonic salts. Dissolve the residue in a little water, filter off a trace of MgO (if any), and test filtrate for potassium by means of $PtCl_4$; a *yellow crystalline* precipitate = **presence of** K; and for sodium, by heating on a platinum wire before the blowpipe flame; a *golden-yellow flame* indicates the **presence of** Na.

QUESTIONS AND EXERCISES.

1. How is magnesic sulphate prepared—1st, from *magnesite*; 2nd, from *dolomite*?
2. Which are the most important magnesium minerals? Give constitutional and graphic formulæ?
3. Explain the action which ammonia, potassic hydrate, and sodic carbonate have upon solutions of magnesic salts in the presence of ammonic salts, and also without them.
4. Describe fully the most characteristic reaction for magnesic salts in the wet way.
5. How is magnesium separated from potassium and sodium?
6. How much crystallized magnesic sulphate, $MgSO_4.7OH_2$, can be prepared from one ton of pure *magnesite*?

CHAPTER III.

REACTIONS OF THE METALS OF GROUP IV.

THIS group comprises the metals BARIUM, STRONTIUM, CALCIUM, which are precipitated by ammonic carbonate from an ammoniacal solution in the presence of ammonic chloride. The latter (if present in sufficient quantity) prevents the precipitation of magnesium.

The three elements barium, strontium, and calcium are scarcely known in a metallic state. They resemble each other very closely in physical and chemical properties, and their compounds are often, indeed generally, found associated in nature.

	Atomic weight.	Sp. gr.	Melting-point.
Ba	136·76	3·75	about that of cast iron.
Sr	87·30	2·54	at a red heat.
Ca	39·91	1·57	at a red heat.

The metals do not appear to be sensibly volatile at the highest furnace temperature. They all decompose water at the ordinary temperature, and oxidize rapidly, superficially, in air. When heated in air or oxygen they burn very brilliantly.

1. **BARIUM**, Ba″. Occurs in nature chiefly in the form of *heavy spar*, $BaSO_4$, and as *witherite*, $BaCO_3$.

REACTIONS IN THE DRY WAY.

Barium compounds, when held in the fusing zone of a Bunsen gas burner, or when heated on thin platinum wire in the inner blowpipe flame, impart a **yellowish-green** colour to the outer flame, especially when treated with strong hydrochloric acid. When viewed through the spectroscope (the chloride* is best employed), two GREEN lines, Baα and Baβ, come out most intensely; Baγ is less marked. Besides these, there are numerous lines in the RED and YELLOW, and one broad indistinct line in the BLUE, close to F of the solar spectrum.

Heavy spar heated on charcoal in the reducing flame is reduced to baric sulphide, BaS, which fuses readily. This reaction is made use of to prepare, on a manufacturing scale, soluble baric salts from the sulphate. Baric carbonate is decomposed only slowly even by ignition to a strong white heat.

REACTIONS IN THE WET WAY.

Baric salts are obtained by dissolving the native carbonate or

---

* The spectra of Ba and of the two following metals are probably those of the *oxides*, and not of the metals themselves.

witherite in dilute acids.* *Heavy spar* is attacked by alkaline carbonates at a high temperature. By mixing, on a small scale, finely powdered baric sulphate with three to four times its weight of fusion mixture, and heating in a platinum crucible over a gas flame, it is converted into baric carbonate, thus:—

$$BaSO_4 + KNaCO_3 = \underset{\text{Insol. in water.}}{BaCO_3} + \underset{\text{Soluble in water.}}{NaKSO_4}.$$

On extracting the fused mass with hot water and filtering, $BaCO_3$ is left, from which, by the addition of the respective acids, small quantities of the different baric salts can be prepared.

The same applies to *celestine*, $SrSO_4$, and to *anhydrite*, $CaSO_4$.

A SOLUTION OF BARIC CHLORIDE, $BaCl_2$, is employed.

Ammonic carbonate (**group-reagent**) precipitates *white* **baric carbonate**, $BaCO_3$, soluble with decomposition in acids; somewhat soluble in ammonic chloride. With carbonic acid it forms a soluble acid carbonate or dihydric dicarbonate, $C_2O_2(HO)_2BaO_2$, but it is reprecipitated, on boiling, with evolution of carbonic anhydride. Baric carbonate is partially decomposed by alkaline sulphates, *e.g.*, potassic sulphate, into baric sulphate and alkaline carbonate. The decomposition is complete in the presence of free carbonic anhydride. $SrCO_3$ and $CaCO_3$ are not changed, not even on boiling with K_2SO_4.

Sodic or potassic carbonate, same precipitate.

KHO and NaHO, free from carbonates and sulphates, which they rarely are, give from highly concentrated solutions a *voluminous* precipitate of **baric hydrate**, $Ba(HO)_2$, soluble in water. A solution of the hydrate in water is known as *baryta-water*. It possesses a strong alkaline reaction, and great affinity for carbonic anhydride.

AmHO gives no precipitate.

H_2SO_4, as well as all **soluble sulphates**, precipitates on boiling, especially in the presence of free acid (dilute HCl), *heavy white* **baric sulphate**, $BaSO_4$, even from very dilute solutions of baric salts. The precipitate is insoluble in water, dilute acids, and alkalies; soluble to a perceptible extent in boiling concentrated hydrochloric and nitric acids, and also in concentrated solutions of ammonic salts, but not if the precipitants are in excess; soluble also in concentrated boiling sulphuric acid, with formation of dihydric baric disulphate, $S_2O_4(HO)_2BaO_2$. The presence of an alkaline citrate greatly interferes with its precipitation. Solutions of strontic or calcic sulphate (two sulphates which are but slightly soluble in water, especially the former) constitute the most delicate tests for barium.

$BaSO_4$ is soluble only in about 400,000 parts of pure water;

---

* Dilute acids (HCl or HNO_3) should be employed, as the baric chloride and baric nitrate, which result from the action of these acids upon witherite, are insoluble in the concentrated acids.

$SrSO_4$ in 7,000 parts of cold water; whilst $CaSO_4$ dissolves in 390 parts of water at 35° C., and in 460 parts at 100° C., being in fact less soluble in hot than in cold water.

HNa_2PO_4 (**hydric disodic phosphate**) gives from neutral or alkaline solutions a *white* precipitate of **hydric baric phosphate**, $HBaPO_4$, readily soluble in dilute nitric, hydrochloric or *acetic* acid. Perceptibly soluble in ammonic chloride.

$\left\{\begin{matrix}COAmO\\COAmO\end{matrix}\right.$ (**ammonic oxalate**) gives from a moderately dilute solution of a baric salt, a *white pulverulent* precipitate of **baric oxalate**, $\left\{\begin{matrix}CO\\CO\end{matrix}\right.BaO_2$ or C_2O_4Ba, soluble in dilute nitric or hydrochloric acid. Soluble also in oxalic and acetic acids when freshly precipitated.

K_2CrO_4 (**potassic chromate**) gives a bright *lemon-yellow* precipitate of **baric chromate**, $BaCrO_4$, even from very dilute *neutral* or *moderately acid* (acetic acid) solutions, readily soluble in nitric, hydrochloric or chromic acid (H_2CrO_4)—reprecipitated by ammonia.—(DISTINCTION FROM STRONTIC AND CALCIC SALTS, WHICH ARE NOT PRECIPITATED FROM DILUTE SOLUTIONS.)

$2HF,SiF_4$ (**hydrofluosilicic acid**) gives a colourless *crystalline* precipitate of **baric silicofluoride**, BaF_2SiF_4, which subsides quickly, especially upon the addition of an equal bulk of alcohol. It is somewhat soluble in water and in dilute acids, insoluble in alcohol. (DISTINCTION OF BARIC FROM STRONTIC AND CALCIC SALTS, WHICH GIVE NO PRECIPITATE EVEN ON THE ADDITION OF ALCOHOL.)

Soluble baric salts, such as baric chloride, nitrate or acetate, constitute exceedingly useful reagents for the detection of acids, on account of the metal barium forming insoluble salts with most acids.

QUESTIONS AND EXERCISES.

1. How can baric sulphate be converted into baric nitrate or chloride?
2. Express in symbolic equations the different reactions for barium.
3. Which are the most delicate reactions for barium?
4. How can barium be separated from strontium and calcium?
5. 1·235 grm. of *witherite* gave ·965 grm. of baric sulphate; what is the percentage of barium and of baric carbonate in the mineral?

2. **STRONTIUM**, Sr''.—Occurs in nature as SULPHATE in the mineral *celestine*, $SrSO_4$; and as CARBONATE in *strontianite*, $SrCO_3$.

EXAMINATION IN THE DRY WAY.

Strontium compounds, when heated on platinum wire in the inner flame, colour the outer flame intensely **crimson**. When the flame is viewed through the spectroscope, it shows a number of characteristic lines, more especially the Srβ and γ lines in the RED and the line Srδ in the BLUE, which latter is particularly suited for the detection of strontium in the presence of Ba and Ca.

Celestine, $SrSO_4$, heated on charcoal in the reducing flame, is converted into strontic sulphide, SrS, from which the chloride may be prepared for blowpipe and other reactions, by treating the residue with hydrochloric acid. *Strontic carbonate*, heated in a platinum crucible, over a gas blowpipe, is almost completely converted into *oxide*, after about 20 minutes' heating.

REACTIONS IN THE WET WAY.

A SOLUTION OF STRONTIC CHLORIDE, $SrCl_2$, is used.

Am_2CO_3 (**group-reagent**) gives a *white* precipitate of **strontic carbonate**, $SrCO_3$, less soluble in ammonic chloride than the corresponding baric carbonate; soluble in dilute acids. Carbonic acid produces the soluble dihydric strontic dicarbonate, $C_2O_2(HO)_2SrO_2$, which is decomposed on boiling into normal carbonate, carbonic anhydride, and water.

Sodic or potassic carbonate, same precipitate.

H_2SO_4, or a **soluble sulphate**, produces a *white* precipitate of **strontic sulphate**, $SO_2SrO_2 = SrSO_4$. From *dilute* solutions a precipitate appears *only after some time*, especially if calcic sulphate be used as the precipitant. Heat assists the precipitation. The precipitate dissolves perceptibly in hydrochloric or nitric acid, but is *insoluble in alcohol.* It is insoluble also on boiling in a concentrated solution of ammonic sulphate, Am_2SO_4, and a little ammonia. (DISTINCTION BETWEEN STRONTIUM AND CALCIUM.)

A solution of strontic sulphate in water is not precipitated by ammonic oxalate, but readily precipitates baric salts.

Na_2HPO_4 (**hydric disodic phosphate**) gives a *white* precipitate of **hydric strontic phosphate**, soluble in acids, including acetic acid.

$\left\{\begin{matrix}COAmO\\COAmO\end{matrix}\right.$ (**ammonic oxalate**) precipitates strontic salts more readily than baric salts. The *white* precipitate of **strontic oxalate**, $\left\{\begin{matrix}CO_2\\CO_2\end{matrix}\right.Sr$ is readily soluble in dilute nitric or hydrochloric acid; somewhat soluble in ammonic salts; but sparingly soluble in oxalic or acetic acid.

QUESTIONS AND EXERCISES.

1. How are strontic chloride and nitrate prepared—1st, from *strontianite*; 2nd, from *celestine*?
2. Which are the most characteristic reactions for strontium?
3. How can strontium be distinguished from barium?
4. How can strontium be separated from calcium?

3. **CALCIUM**, Ca''.—Occurs in nature in the mineral, vegetable, and animal kingdoms, in vast masses, in combination with carbonic, sulphuric, silicic and phosphoric acids. In plants it occurs combined with carbonic, sulphuric, and phosphoric acids; in animals combined with phosphoric and carbonic acids. It is occasionally also found in minerals which result from the action of acids (such as nitric or arsenic acid) upon *calc spar.*

The principal calcium minerals are the various CALCIC CARBONATES, differing in physical properties or in crystalline structure, such as *calc spar*, $CaCO_3$ (containing occasionally barium, magnesium, iron, manganese, lead, in variable proportions, and passing gradually into *baryto-calcite* and *dolomite*, *siderite*, *diallogite*, and *plumbo-calcite*), *arragonite*, *marble*, *limestone*, *chalk*; the SULPHATES, such as *gypsum*, $SO_2(HO)_4Ca$, *anhydrite*, $CaSO_4$, *alabaster*, *selenite*; the PHOSPHATES, such as *apatite*, $P_3O_3(CaO_2)_4\left(\genfrac{}{}{0pt}{}{O}{F}Ca''\right)'$, or $3(3CaO.P_2O_5) + CaCl_2$, some contain both chlorine and fluorine; *bone-earth*, $Ca_3P_2O_8$, and *fluor spar*, CaF_2.

REACTIONS IN THE DRY WAY.

Most calcium compounds, when heated in the inner flame of the blowpipe, colour the outer flame **yellowish-red**; calcic phosphate and borate excepted. The presence of strontium entirely obscures the calcium reaction. The lime *spectrum* shows, among other lines in the RED and YELLOW, an intensely **green** line, $Ca\beta$, also an intensely **orange** line, $Ca\alpha$. It requires a very good spectroscope to see the faint **indigo-blue** line to the right of G in the solar spectrum.

Calcic carbonate when strongly ignited becomes converted into caustic or quicklime, CaO, which reacts alkaline. It combines with water very eagerly, evolving much heat, and is converted into calcic hydrate, $Ca(HO)_2$ (slaked lime), which is less soluble in water than either baric or strontic hydrate. It is also more soluble in cold than in hot water. Calcic sulphate is converted into calcic sulphide, CaS, when ignited on charcoal in the reducing flame. The mass reacts likewise alkaline.

REACTIONS IN THE WET WAY.

Calcic salts are readily prepared from pure *calc spar* or *marble*, by means of dilute acids.

A SOLUTION OF CALCIC CHLORIDE, $CaCl_2$, is used.

Ammonic carbonate (**group-reagent**) precipitates *white* **calcic carbonate**, $CaCO_3$, which is bulky and amorphous at first, but on warming gently becomes rapidly crystalline. Calcic carbonate is somewhat soluble in ammonic chloride, especially when freshly precipitated. It is in fact partially reconverted on boiling into calcic chloride.

Sodic or potassic carbonate, same reaction.

H_2SO_4, or a **soluble sulphate**, precipitates from concentrated solutions of a calcic salt *white* **calcic sulphate**, $SO_2(HO)_2CaO = CaSO_4H_2O + Aq.$, soluble in much water, and still more soluble in acids. A precipitate is obtained on the addition of twice the volume of alcohol from solutions which are too dilute to be precipitated by sulphuric acid or by a soluble sulphate. Calcic sulphate dissolves readily on boiling in a concentrated solution of ammo sulphate.

A solution of calcic sulphate precipitates both baric and strontic salts.

HNa_2PO_4 (**hydric disodic phosphate**) gives a *bulky white* precipitate of **tricalcic phosphate**, $Ca_3P_2O_8$, soluble in dilute hydrochloric or nitric acid, and soluble in acetic acid; reprecipitated by ammonia.

$\left\{\begin{matrix}COAmO\\COAmO\end{matrix}\right.$ (**ammonic oxalate**) produces even from very dilute solutions of calcic salts a *white pulverulent* precipitate of **calcic oxalate**, $\left\{\begin{matrix}COO\\COO\end{matrix}\right.Ca$ + Aq., readily soluble in hydrochloric or nitric acid; not perceptibly soluble in oxalic or acetic acid. On gentle ignition calcic oxalate breaks up into calcic carbonate, and carbonic oxide gas, and on igniting very strongly, caustic lime is left.

Soluble calcic salts, such as the chloride or nitrate, constitute important reagents for the detection of organic acids, on account of the metal calcium forming insoluble salts with many of them.

QUESTIONS AND EXERCISES.

1. Which are the most important natural lime compounds?
2. Give graphic formulæ for *gypsum, anhydrite, calc spar, fluor spar, apatite.*
3. Which are the most delicate reactions for calcium in the wet way?
4. Calculate the percentage composition of *bone ash.*

Separation of Barium, Strontium, and Calcium.—Barium minerals frequently contain strontium and calcium, and strontium minerals barium and calcium as well. A method of separating these metals is based upon—

1st. The *insolubility* of $BaCl_2$ in *absolute alcohol* ($SrCl_2$ and $CaCl_2$ being soluble).

2nd. The *insolubility* of $Ba(NO_3)_2$, and $Sr(NO_3)_2$ in *absolute alcohol* (calcic nitrate being soluble).

A hydrochloric acid solution of the mineral containing Ba and Sr, or Sr and Ca, or possibly Ba, Sr, and Ca, is prepared, and the solution evaporated to dryness and gently ignited. (Strong ignition must be avoided, as $CaCl_2$ is slightly decomposed into an insoluble basic salt.)

Barium is separated from strontium and calcium, by digesting the finely divided residue with absolute alcohol, and separating the undissolved $BaCl_2$ by filtration.

Strontium is separated from calcium by evaporating or distilling off the absolute alcohol, which contains the $SrCl_2$ and $CaCl_2$; precipitating with ammonic carbonate, filtering, and conversion of the strontic and calcic carbonates into nitrates by means of dilute nitric acid. The solution of the two nitrates is evaporated to dryness on a water-bath and absolute alcohol added, when calcic nitrate is dissolved out, strontic nitrate being insoluble in absolute alcohol.

The presence of these metals may be confirmed by setting fire to the alcoholic solution containing baric, strontic, or calcic chloride (or nitrate); the alcohol is seen to burn with the characteristic colour observed when traces of these salts were heated on a platinum wire.

Several other methods for recognizing and separating the metals of Group IV will suggest themselves.

It is often useful to ascertain whether one or two, or all the metals of this group are present in a solution. This can be done by adding to their *neutral* solution a solution of CrO_2KO_2, (K_2CrO_4), or $2HF,SiF_4$. A yellow or a transparent crystalline precipitate indicates barium. To a portion of the filtrate add calcic sulphate, SO_2CaO_2'',($CaSO_4$); a precipitate forms perhaps only after some time, proving the presence of strontium; or the solution remains clear, in which case calcium only need be looked for, the presence of which is indicated by the precipitate which ammonic oxalate produces from another portion of the *largely diluted* solution. If both strontium and calcium are present, separation becomes desirable.

No difficulty will be experienced by the student in drawing up schemes of analysis based upon—

1st. The *insolubility of* $BaCl_2$ and $Sr(NO_3)_2$ *in absolute alcohol.*

2nd. The *insolubility of* $BaCl_2$ *in absolute alcohol* and *that of* SO_2SrO_2 *in a concentrated solution of* $SO_4(NH_4)_2$.

3rd. The *insolubility of* BaF_2,SiF_4, or $BaCrO_4$, *as well as of* SO_2SrO_2 *in water; calcic sulphate being sufficiently soluble to be readily indicated by ammonic oxalate.*

CHAPTER IV.

REACTIONS OF THE METALS OF GROUP III, OR AMMONIC SULPHIDE GROUP.

GROUP III comprises the metals NICKEL, COBALT, MANGANESE, ZINC, IRON, CHROMIUM, ALUMINIUM, likewise the phosphates of these metals, and of MAGNESIUM, BARIUM, STRONTIUM, and CALCIUM.

1. Add to a solution* containing cobalt nitrate, ferric chloride, and calcic phosphate, dissolved in a little dilute hydrochloric acid, a concentrated solution of ammonic chloride, and then ammonia. A precipitate is produced. Filter, and add to the filtrate ammonic sulphide. A further precipitation takes place; the precipitate is black.

This shows *that some members of this group are precipitated by AmCl and AmHO; others only on the addition of* SAm_2.

2. Add to a solution of ferric, chromic, and aluminic chlorides (Fe_2Cl_6, Cr_2Cl_6, and Al_2Cl_6) ammonic chloride and ammonia, till it is just distinctly ammoniacal, and boil for a few minutes. A bulky gelatinous precipitate is obtained. Filter. Add to the clear filtrate a few drops of ammonic sulphide: no further precipitation takes place.

Showing *that Iron, Chromium, and Aluminium are precipitated (as hydrates) from their saline solutions by AmCl and AmHO alone, without the aid of* SAm_2. (Ammonic chloride has no share in the precipitation, but counteracts the solubility of the aluminic hydrate in excess of the precipitant, and prevents the precipitation of magnesium as hydrate, if present in the solution.)

3. Dissolve some baric, strontic, calcic, and magnesic phosphates in dilute hydrochloric acid, and cautiously add to the solution ammonia. No precipitate is produced till the free acid has been neutralised (with formation of ammonic chloride), when the phosphates are reprecipitated. Filter and add ammonic sulphide to the filtrate. No further precipitation takes place.

This shows *that the phosphates of the alkaline earthy metals are precipitated by ammonia alone.*

4. Dissolve some phosphates of Ni, Co, Mn, Zn, and Fe^{iv} in dilute hydrochloric acid.† To one portion of the solution add ammonic chloride and ammonia. A precipitate is formed. The phosphates are reprecipitated. Filter and add ammonic sulphide; a further precipitate is produced.

Showing *that the phosphates of these metals are not entirely precipitated by ammonic chloride and ammonia.*

---

* Solutions containing ·005 grm. of the metal in every c.c. are readily prepared, and should be kept for use. 5 c.c. of each solution will be found a convenient quantity.

† This solution may also be prepared by adding hydric disodic phosphate to solutions of the above metals as long as a precipitate forms, and dissolving the precipitate in a little hydrochloric acid.

Thus far it will be seen that these two reagents precipitate:—

Nickelous phosphate
Cobaltous ,,
Manganous ,,
Zincic ,,
Ferric ,,
Ferric hydrate
Chromic ,,
Aluminic ,,

Chromic phosphate
Aluminic ,,
Baric ,,
Strontic ,,
Calcic ,,
Magnesic ,,

5. To a solution of the sulphates or chlorides (free from Fe) of Ni, Co, Mn, and Zn, add AmCl in considerable excess, and then AmHO in slight excess. No precipitate is obtained, the precipitate first produced by AmHO being soluble in the ammonic salt. To one portion of the solution add strong sulphuretted hydrogen water (or pass a current of sulphuretted hydrogen gas); a copious precipitate is produced, consisting of NiS and CoS (black), ZnS (white), and MnS (pale pink).

This shows *that Nickel, Cobalt, Manganese, and Zinc salts are not precipitated by AmCl and AmHO, but by SAm_2.*

On exposing the other portion of the solution for some time to the air, it is seen to turn turbid where it is in contact with the air. Heat and shake the solution and the turbidity increases rapidly.

Showing *that AmCl and AmHO produce, under favourable conditions, a partial precipitation.*

6. To another portion of the solution of the phosphates of Ni, Co, Mn, Zn, and Fe (see 4), add AmCl, AmHO, and SAm_2, without first separating by filtration the precipitate produced by AmCl and AmHO. THE PHOSPHATES OF Co, NI, MN, ZN, and FE, which may be represented in the hydrochloric acid solutions, ARE DECOMPOSED INTO SULPHIDES, AND AMMONIC PHOSPHATE IS LEFT IN SOLUTION.

7. To a solution of Fe_2Cl_6 add AmCl and AmHO. A reddish-brown precipitate of ferric hydrate, $Fe_2(HO)_6$, is produced, which on the addition of SAm_2 turns instantaneously black.

This shows *that iron is first precipitated as hydrate, and is subsequently converted into sulphide.* Chromic and aluminic chlorides are precipitated under the same circumstances as hydrates, but they form no sulphides in the wet way.

It will thus be seen that the group-reagents AmCl and AmHO, for reasons stated under 4 and 5, cannot thoroughly separate some of the members of Group III from others, and that SAm_2 should invariably be added as well. The three reagents* precipitate:—

---

* Add AmHO to a solution of baric, strontic, calcic (and magnesic) oxalates in dilute hydrochloric acid, as long as a white precipitate is obtained. The oxalates of the alkaline earths are reprecipitated more or less completely as soon as the hydrochloric acid which (as in the case of the corresponding phosphates) holds them in solution is completely neutralised.

The same applies to the fluorides, borates, tartrates, citrates, &c., of these

1. SULPHIDES—

NiS	black
CoS	black
MnS	pale pink
ZnS	white
FeS	black.

2. HYDRATES—

$Cr_2(HO)_6$	green
$Al_2(HO)_6$	white.

3. PHOSPHATES of Cr, Al, Ba, Sr, Ca, and Mg.

NICKEL, Ni'' and ^{iv}.—Occurs in nature as SULPHIDE, NiS'', in *capillary pyrites*, *hair nickel*, or *millerite;* as ARSENIDE, in *arsenical nickel*, $\left\{\begin{array}{l}{}''As' \\ {}''As'\end{array}\right.Ni''$, and in *copper nickel*, $\left\{\begin{array}{l}'As''Ni'' \\ 'As''Ni''\end{array}\right.$; as ANTIMONIDE, in $\left\{\begin{array}{l}'Sb''Ni'' \\ 'Sb''Ni''\end{array}\right.$, *antimony nickel*, combined with SULPHIDE, as in *nickel glance* or *grey nickel ore*, $\left\{\begin{array}{l}{}''As' \\ {}''As'\end{array}\right.Ni,Ni^{iv}S_2$, as *antimony nickel glance*, $\left\{\begin{array}{l}{}''Sb' \\ {}''Sb'\end{array}\right.Ni,Ni^{iv}S_2$; also in the form of minerals, which are the result of the oxidation of other nickel minerals, *e.g.*, as *nickel ochre*, $As_2O_2(NiO)_3$, and *emerald nickel*, $CO(ONi''HO)_2NiO,5OH_2$.

The metal nickel is very hard and exhibits a slight yellow tint on a fresh or polished surface. Its atomic weight = 57·93, specific gravity = 8·9, melts between 1450° and 1600° C. It does not oxidise appreciably at ordinary temperatures in air or in contact with water, but acts upon acids readily. It becomes decidedly magnetic.

REACTIONS IN THE DRY WAY.

When nickel compounds are heated on charcoal with dry sodic carbonate in the *inner* blowpipe flame, they are reduced to a grey

---

earthy bases, which are precipitated by AmHO, although in the presence of much AmCl they are to a great extent held in solution.

Silicic acid and silicates, soluble in hydrochloric acid, are likewise acted upon by AmCl and AmHO, gelatinous silica, and silicates, being precipitated.

In order to avoid complicating the qualitative course, it is usually preferred to evaporate the hydrochloric acid filtrate from Group II to complete dryness, with the addition, towards the end of the evaporation, of a little concentrated nitric acid, whenever AmCl and AmHO produce a precipitate. By these means silicic anhydride, SiO_2, is left behind insoluble in acids; the fluorides and borates are for the most part decomposed; boric and hydrofluoric acid being set free or volatilised. Oxalates are destroyed with evolution of carbonic anhydride by the oxidizing action of the nitric acid; and tartrates, etc., are broken up by gentle ignition into carbon and volatile gaseous products; ferrous salts are converted into ferric salts, and on extracting the ignited residue with a little concentrated hydrochloric acid, the metals are obtained in solution as chlorides, together only with the phosphates of the alkaline earths, earthy and metallic bases.

metallic powder which is magnetic. Heated on a *borax* bead, in the *outer* flame, nickel compounds yield an intensely coloured glass, which appears **hyacinth-red to violet-brown** when hot, and **yellowish to sherry-red** when cold (according to the quantity of nickel present). On fusing a little nitre in the bead, the colour is changed to blue or dark purple, whereby nickel compounds may be distinguished from iron. Heated in the *reducing* flame the colour disappears, and the bead assumes a turbid grey appearance, owing to finely divided particles of metallic nickel. The reactions with microcosmic salt are similar, but the bead becomes almost colourless when cold.

REACTIONS IN THE WET WAY.

A SOLUTION OF NICKELOUS SULPHATE, $NiSO_4 = SO_2(O_2Ni)''$ is employed.

Solutions of salts of nickel are generally *green;* those of cobalt *red.* A solution of cobaltous chloride turns *blue* on heating. A solution of both a nickel and a cobalt salt is *red*, *green*, or *colourless*, according to the quantities present of each of the metals in solution.

SAm_2 (**group-reagent**) gives a *black* precipitate of **nickelous sulphide**, NiS, slightly soluble in excess of the reagent, especially in the presence of free ammonia or of *yellow* ammonic sulphide, forming a dark brown solution, whence the sulphide is reprecipitated on boiling. The presence of ammonic chloride (or better still, ammonic acetate) assists the precipitation. Nickelous sulphide dissolves with difficulty in dilute hydrochloric acid, readily in nitric acid or aqua regia, and is but slightly soluble in acetic acid.

SH_2 gives no precipitate in acid solution, and a partial precipitate only from a salt of nickel with a mineral acid; but produces readily a precipitate from a solution of nickelous acetate, or a nickelous salt mixed with an alkaline acetate, especially on heating.

NaHO or KHO precipitates *an apple-green* **hydrate**, $Ni(HO)_2$, insoluble in excess, soluble in ammonic salts to a greenish-blue fluid. Nickelous hydrate leaves on ignition nickelous oxide. It does not absorb oxygen from the air.

AmHO produces a slight *greenish* precipitate, readily soluble to a blue fluid. No precipitate in presence of ammonic chloride.

Sodic carbonate precipitates an *apple-green* **basic carbonate,** varying in composition.

Ammonic carbonate same precipitate, readily soluble in excess, when filtered and washed, to a greenish-blue solution.

KCy (free from cyanate (CyKO) and carbonate*) gives a *yellowish-green* precipitate of **nickelous cyanide,** $NiCy_2$, which dissolves readily in excess of potassic cyanide to a brownish-yellow solution, containing a double cyanide of nickel and potassium, $2KCy,NiCy_2$. On adding a dilute acid (HCl or H_2SO_4), $NiCy_2$ is reprecipitated, and KCy is decomposed with evolution of HCy. Boiling with hydrochloric acid decomposes the nickelous cyanide likewise.

---

* It is preferable to add hydrocyanic (prussic) acid, HCy, to a neutral solution of a nickelous salt, and then KHO drop by drop, till the yellowish-green precipitate is redissolved. Great caution has to be observed on account of the highly poisonous nature of HCy.

The solution of the double cyanide is not altered by boiling with excess of HCy, but the nickelous salt is oxidised in the cold by chlorine or bromine water or the addition of a *concentrated* solution of sodic hypochlorite, $ClNaO$, to *black* **nickelic hydrate**, $'Ni''_2(HO)_6$, which is gradually precipitated; thus:—

$$2NiCy_2 + ClNaO + 5OH_2 = Ni_2(HO)_6 + NaCl + 4HCy.$$

Nickelic hydrate may also be obtained by passing chlorine through water in which nickelous hydrate is suspended. HCl decomposes the tetrad nickel compound into nickelous chloride and free chlorine. Nickelic oxide, Ni_2O_3, obtained by igniting the hydrate, or by keeping the nitrate at a temperature of about 200° C., is a black substance, scarcely soluble in boiling *acetic acid.*

QUESTIONS AND EXERCISES.

1. Express in symbolic equations the reactions for nickel in the wet way.
2. State which are the principal nickel minerals, and translate into graphic formulæ the constitutional formulæ of *emerald nickel*, *antimony nickel*, nickelous nitrate, and arsenate.
3. Calculate the percentage composition of *capillary pyrites.*

COBALT, Co'' and ^{iv}.—Occurs in nature as SULPHIDE, or *cobalt pyrites*, Co_2S_3 or $\left\{\begin{matrix} CoS'' \\ CoS'' \end{matrix}\right. S''$; as arsenide in $\left\{\begin{matrix} ''As' \\ ''As' \end{matrix}\right. Co''$, tin-white cobalt or *smaltine* (*speiss cobalt*), as SULPHARSENIDE or *cobalt glance*, $\left\{\begin{matrix} ''As' \\ ''As' \end{matrix}\right. Co'',Co^{iv}S_2$; also in the form of products of oxidation, such as *cobalt vitriol*, $SO_2(HO)_2CoO,6OH_2$, as *arsenate*, $CoAs_2O_8,8OH_2$, in *cobalt bloom.* Cobalt is generally found in small quantity in most nickel and iron ores. It resembles the metal nickel very closely, so much so that it may almost be looked upon as an isomeric form of that element. Its atomic weight = 58·89. Specific gravity = 8·6. Melts at about 1800° C. It is slightly redder in tint than Ni, and oxidizes more readily on exposure to air or water. Acids act upon it about as readily as in the case of nickel. It also becomes slightly magnetic.

REACTIONS IN THE DRY WAY.

Cobalt is usually detected with comparative facility. Cobalt minerals containing sulphur or arsenic are roasted on charcoal, or in a glass tube, when sulphurous and arsenious anhydrides are evolved. The residue is then introduced into a *borax* bead, and heated in the *outer* flame, when a *fine* **blue**, so-called cobalt glass is obtained. This colour remains the same both in the outer and inner, or *reducing* flame. In cases where much Mn, Fe, Cu, or Ni are mixed with Co, the blue appears distinctly only after the bead has been heated for some time in the reducing flame. Microcosmic salt gives the same blue bead. Heated on charcoal, with sodic carbonate, in the reducing flame, cobalt separates as a grey metallic powder, which is attracted by the magnet.

REACTIONS IN THE WET WAY.

Use A SOLUTION OF COBALTOUS NITRATE, $\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\{Co\begin{matrix}O\\O\end{matrix}\Big)$, or chloride, $CoCl_2$.

SAm_2 (**group-reagent**) gives a *black* precipitate of **cobaltous sulphide**, CoS, insoluble in excess of the reagent, scarcely soluble in acetic acid, and very difficultly soluble in dilute hydrochloric or sulphuric acid, but readily soluble in aqua regia upon the application of heat. Hence a black residue left, on treating the ammonic sulphide precipitate of Group III with dilute hydrochloric acid, indicates probably the presence of cobaltous or nickelous sulphide.

SH_2 gives no precipitate from an acid solution, but precipitates cobaltous sulphide partially from a neutral solution, and wholly from a solution of cobaltous acetate, or from a solution of cobaltous salt containing a mineral acid, on the addition of an alkaline acetate, and upon heating.

KHO or NaHO gives a precipitate of a *blue* **basic salt**, which turns *olive-green* on exposure to air, owing to the absorption of oxygen. On heating in very dilute solutions, a *rose-red* **cobaltous hydrate**, $Co(HO)_2$, is obtained, which, however, often contains a small amount of dark brown cobaltic hydrate. Ammonic carbonate dissolves the precipitate (after filtration and washing) to an intensely violet-red fluid.

By suspending cobaltous hydrate in water, and passing a current of chlorine into it, black cobaltic hydrate is precipitated, whilst cobaltous chloride remains in solution, thus:—

$$3Co(HO)_2 + Cl_2 = \underset{\substack{\text{Cobaltic}\\\text{hydrate.}}}{Co_2(HO)_6} + CoCl_2.$$

In the presence of an alkali (NaHO) the whole of the cobaltous hydrate is converted into cobaltic hydrate.

AmHO produces in neutral solutions a slight precipitate of a **basic salt**, which dissolves readily in excess. The solution is reddish-brown. Ammonic chloride prevents the precipitation altogether. The solution absorbs oxygen from the air, and becomes red on standing.

Sodic carbonate precipitates a *peach-coloured* **basic carbonate.**

Ammonic carbonate, same precipitate; readily soluble, however, in excess, to a red solution.

KCy gives with all normal cobaltous salts a *brownish-white* precipitate of **cobaltous cyanide**, $CoCy_2$, soluble in excess, reprecipitated by dilute hydrochloric or sulphuric acid.

If the cobaltous solution, however, contains free acid, so as to liberate hydrocyanic acid by the action of the latter upon the excess of KCy, and if the solution containing the double cyanide $2KCy, CoCy_2$, be heated for some time, dilute hydrochloric or sulphuric acid no longer produces a precipitate, the whole of the cobaltous cyanide having been converted into cobaltic cyanide, $'Co'''_2Cy_6$, which remains combined with 6KCy to form a well-defined and stable salt, called **potassic cobalticyanide**, $K_6Co_2Cy_{12}$, hydrogen being evolved, thus:—

$$
\begin{aligned}
2CoCy_2 + 2HCy &= Co_2Cy_6 + H_2. \\
6KCy + Co_2Cy_6 &= K_6Co_2Cy_{12}.
\end{aligned}
$$

Potassic
cobalticyanide.

This salt is not acted upon by sodic hypochlorite in the cold.

Separation of Nickel from Cobalt.—It is obvious that the hydrocyanic acid reaction is a method of separation of nickel from cobalt. To a *neutral* solution of the two salts add cautiously, drop by drop, a solution of potassic cyanide as long as a precipitate forms, and till the precipitate is just redissolved and the yellowish-brown turbid liquid has become clear. Heat gently for some time in a well-ventilated closet, allow to cool, and add a *concentrated* solution of sodic hypochlorite. $Ni_2(HO)_6$ is precipitated in the cold, and cobalt remains in solution as $K_6Co_2Cy_{12}$. Separate by filtration. Test the residue before the blowpipe for nickel, and evaporate the solution to dryness, and test for cobalt by means of a borax bead.

Instead of separating nickel as $Ni_2(HO)_6$ by means of ClNaO or Br water, the solution, after digesting with excess of HCy or KCy, may also be precipitated whilst hot with finely divided freshly precipitated **mercuric oxide.** On digesting for a short time at a gentle heat, the whole of the nickel is precipitated, partly as $Ni(HO)_2$, partly as $NiCy_2$, the mercury combining with the liberated cyanogen. Filter off the *greenish* or *yellowish-grey* precipitate, wash, and ignite. Pure NiO is left; thus:—

$$(1)\ 2NiCy_2 + xHgO + OH_2 = HgCy_2 + Ni(HO)_2,NiCy_2 + x - 1HgO.$$

Greenish
precipitate.

$$(2)\ Ni(HO)_2,NiCy_2 + HgO = 2NiO + HgCy_2 + OH_2.$$

Volatile
on ignition.

The cobalt remains in the solution as $K_6Co_2Cy_{12}$. Nearly neutralize with dilute nitric acid, and add a neutral solution of mercurous nitrate, $Hg_2(NO_3)_2$. A white precipitate of **mercurous cobalticyanide**, $(Hg''_2)_3Co_2Cy_{12}$, forms, which contains the whole of the cobalt. Filter, wash, and ignite under a hood with free access of air, when **tricobaltic tetroxide**, Co_3O_4, is left.

Another method of separation consists in adding a concentrated solution of $NOKO = (KNO_2)$ (**potassic nitrite**) in considerable excess to a concentrated neutral solution of the two metals, then acetic acid in sufficient quantity to freely redissolve the precipitate, which is at first produced by the free KHO and potassic carbonate, contained as impurities in the potassic nitrite. On keeping the solution in a moderately warm place, the nickel salt remains in solution, and the whole of the cobalt separates in the form of a crystalline precipitate of a *fine yellow* colour (from a dilute solution only after long standing), the formation of which is expressed by the equation :—

$$2\,{}^{NO_2}_{NO_2}Co^{O}_{O} + 14NO_2K + 4\left\{\begin{matrix}CH_3\\ COHO\end{matrix}\right. + OH_2 = \underset{\text{Yellow}}{Co_26(NO_3),}$$

$$\underset{\text{precipitate.}}{6NOKO,3OH_2} + 4NO_3KO + 4\left\{\begin{matrix}CH_3\\ COKO\end{matrix}\right. + N_2O_2.$$

The precipitate is perceptibly soluble in cold, and more readily still in hot water; it is decomposed by hot nitric or hydrochloric acid, or by potassic hydrate; insoluble in alcohol; insoluble in the presence of potassic acetate; and it can therefore be washed by a solution of potassic acetate, and finally with alcohol. This REACTION SEPARATES NICKEL FROM COBALT VERY EFFECTUALLY.

From the filtrate the nickel is best precipitated as an apple-green basic carbonate by a fixed alkaline carbonate.

The presence of Ba, Sr, or Ca salt interferes with the reaction, as it gives rise to the precipitation of triple nitrites of Co, Ni, and another metal.

On igniting a small quantity of $N_2O_4NiO_2$, a dirty greyish powder of NiO is left. Ignite next $N_2O_4CoO_2$ (gently at 202° C.) and black cobaltous dicobaltic tetroxide, $Co_3O_4 = \left\{\begin{matrix}CoO\\ CoO\end{matrix}\right.(CoO_2)$, is left, which is *not* soluble in boiling dilute acetic acid. On treating this oxide with hydrochloric acid, chlorine gas is evolved, according to the equation :—

$$Co_3O_4 + 8HCl = 3CoCl_2 + Cl_2 + 4OH_2.$$

Both nickel and cobalt are capable of forming compounds in which the metals exist in a **tetrad** condition, viz.,

$$Ni_2O_3, \text{ or } \underset{\substack{\text{Nickelic}\\ \text{oxide.}}}{\left\{\begin{matrix}NiO\\ NiO\end{matrix}\right.O}, \text{ and } Co_2O_3, \text{ or } \underset{\substack{\text{Cobaltic}\\ \text{oxide.}}}{\left\{\begin{matrix}CoO\\ CoO\end{matrix}\right.O}; \text{ or } \underset{\substack{\text{Cobaltic}\\ \text{sulphide.}}}{Co_2S_3.}$$

Ni_2O_3 is, however, mostly obtained in the wet way by the action of oxidizing agents, and cannot exist at a high temperature.

Co_3O_4, on the other hand, is obtained in the dry way, or on gentle ignition of cobaltous salts containing volatile acids, and gives up a portion of its oxygen only on strong ignition.

The same tendency to form a compound in which cobalt exists as a tetrad element is observed on exposing the freshly-precipitated hydrate to the air, or on passing chlorine or adding bromine or iodine to cobaltous solutions.

Little use has been made of these reactions beyond the conversion of $CoCy_2$ into Co_2Cy_6 in the presence of potassic cyanide, or of CoO into Co_2O_3 in the potassic nitrite reaction.

QUESTIONS AND EXERCISES.

1. Translate into graphic formulæ the constitutional formulæ of *cobalt pyrites*, *[illegible]*, *cobalt bloom*, cobaltic cyanide.
2. How is Co separated from Ni?
3. 2 grms. of an ore containing Ni and Co yield ·[illegible] grm. of NiO and ·1575 grm. of Co_3O_4: what is the percentage of Ni and Co in the ore?
4. How would you prepare potassic cobalticyanide?

MANGANESE, Mn, [illegible] and [illegible].—Occurs in nature in various states of oxidation, forming oxides, of which the mineral *pyrolusite*, MnO_2, is the most important. It is found in small quantities in many iron ores, and is a frequent constituent of SILICATES: the MnO replacing the isomorphous bases FeO, ZnO, MgO, CaO, without altering the crystalline structure of the minerals. It exists with [illegible] in [illegible] in manganous and manganic oxides. The ANHYDROUS OXIDES known, besides pyrolusite, are *braunite*, $MnOMnO_2$, or Mn''_2O_3, *hausmannite*, $\begin{matrix}MnO\\MnO\end{matrix}Mn\begin{matrix}O\\O\end{matrix}$, or Mn''_3O_4; the HYDRATES are: *manganite*, $\left\{\begin{matrix}MnOHO\\MnOHO\end{matrix}\right.$ *psilomelane*, $\begin{matrix}Mn(HO)_2\\Mn(HO)_2\end{matrix}Mn\begin{matrix}O\\O\end{matrix}$ and $\begin{matrix}MnHO_2\\MnHO_2\end{matrix}Mn=\begin{matrix}O\\O\end{matrix}$, *varvicite*, $\left\{\begin{matrix}Mn\ O\\MnO(O_2Mn''(HO)_2)'',\\Mn\ O\end{matrix}\right.$ *copper manganese*, $\left\{\begin{matrix}MnHO_2\\O\\MnHO_2\end{matrix}\right.Cu=\begin{matrix}O\\O\end{matrix}$ Manganese is found in combination with sulphur in *manganese blende*, MnS; with CARBONIC ACID, as *diallogite*, $MnCO_3$; with silica in *red manganese* or *mangankiesel* (*rhodonite*), SiO_3Mn, and in *tephroite*, $SiMn_2O_4$; with PHOSPHORIC ACID, as *triplite*, $P_2O_5(MnO)_3(FeO)_3 = P_2O_8Mn_3Fe_3$.

Manganese is not used in the metallic state, and very little is known of it. It is mostly employed as an alloy with iron, *spiegeleisen*, etc. Its atomic weight = 53·91. Specific gravity = [illegible]. It melts at about 1900° C., therefore higher than iron. It oxidises very rapidly in air and water, and dissolves in most acids.

EXAMINATION IN THE DRY WAY.

The presence of manganese is readily detected in minerals which contain no other oxides capable of colouring fluxes, as they dissolve when heated in the *outer* flame, in the *borax* bead, or in a bead of microcosmic salt, to a clear VIOLET-RED pearl, which becomes of a fine **amethyst** colour on cooling. The bead becomes **colourless** when heated in the *reducing* flame. If other metallic oxides are present, it is preferable to mix a small trace of the finely powdered manganese compound with two or three times its weight of sodic carbonate (a little nitre may likewise be added), and to fuse on platinum foil (a small platinum spoon or the lid of a platinum crucible) in the oxidising flame, when a **bluish-green mass** is left after cooling, consisting of **sodic manganate**, $MnO_2(NaO)_2$. The mass at the same time loses its transparency. THIS FORMS THE MOST CHARACTERISTIC REACTION FOR MANGANESE. Manganous and manganic oxides are converted into a higher oxide, $Mn^{vi}O_3$, in which Mn exists as a hexad.

EXAMINATION IN THE WET WAY.

All the higher oxides of manganese, when heated with hydrochloric acid, evolve chlorine, and are converted into manganous chloride. The chlorine so evolved becomes the measure of the amount of MnO_2 present in a manganese ore.

A SOLUTION OF MANGANOUS CHLORIDE, $MnCl_2$ (free from Fe) may be employed.

Dilute solutions of pure manganous salts (free from manganate or permanganate) are colourless.

SAm_2 **(group-reagent)** gives a *flesh-coloured* precipitate of **manganous sulphide**, MnS, readily soluble in dilute acids, even acetic acid. Hence the presence of free acetic acid prevents the precipitation of manganese (METHOD OF DISTINGUISHING Co AND Ni FROM Mn). The manganese may be separated by repeating once or twice the precipitation of cobalt and nickel in the presence of acetic acid.

SH_2 does not precipitate a neutral solution of a manganous salt; the acetate even is precipitated very slowly and imperfectly, and not at all when free acetic acid is present.

KHO or NaHO gives a *white* precipitate of **manganous hydrate**, $Mn(HO)_2$, insoluble in excess. The precipitate speedily absorbs oxygen from the air, and turns dark brown with formation of $\left\{\begin{matrix} MnOHO \\ MnOHO \end{matrix}\right.$, when it no longer dissolves completely in ammonic chloride.

AmHO precipitates a *white hydrate* from neutral solutions; insoluble in excess, or in ammonic carbonate.

No precipitate is produced in solutions containing ammonic chloride. On exposing an ammoniacal solution of the soluble double chloride, $2AmCl,MnCl_2$, to the action of the air, the who of the manganese is gradually precipitated as dark brown [illegible]

ganic dioxydihydrate, $\left\{\begin{matrix}MnOHO\\MnOHO\end{matrix}\right.$. This reaction is characteristic for manganese compounds.

AmHO conveys in this change oxygen to the manganous salt in a manner similar to the action it has upon cobaltous salts, or upon metallic copper, in the presence of oxygen or air.

Owing to this tendency of manganous salts to become oxidized and precipitated in the presence of AmHO, it is all but impossible to separate manganous from ferric salts by means of AmCl and AmHO. The reddish-brown ferric hydrate, which is precipitated, invariably carries down more or less $\left\{\begin{matrix}MnOHO\\MnOHO\end{matrix}\right.$; and *small quantities of manganese cannot, therefore, be separated from iron by precipitation with AmCl and AmHO.* The separation succeeds best if the excess of ammonia be *immediately* boiled off.

Sodic or potassic carbonate precipitates *white* **manganous carbonate**, $MnCO_3$, insoluble in excess of the reagent, but pretty readily soluble in ammonic chloride. This precipitate absorbs likewise oxygen from the air, and turns to a dirty brownish-white colour, owing to the formation of dimanganic dioxydihydrate. On ignition with free access of air, the white carbonate turns first black, and changes subsequently to brown **trimanganic tetroxide,** Mn_3O_4. All manganese oxides are obtained upon ignition in the air in the form of Mn_3O_4.

KCy gives a *whitish* precipitate of **manganous cyanide**, $MnCy_2$, soluble in excess to a brown solution, which is not precipitated by SAm_2.

It has just been seen how readily manganous compounds are converted, more or less completely, into higher oxides, in which manganese acts the part of a tetrad element. In the brown hydrated dioxide, obtained when a manganous salt is digested with sodic hypochlorite, according to the equation :—

$$MnCl_2 + ClNaO + 2OH_2 = Mn^{iv}O(HO)_2 + NaCl + 2HCl,$$

the manganese exists likewise as a tetrad element. By fusion in the dry way with sodic carbonate, alone or together with nitre, the manganous or manganic compounds are converted into an alkaline manganate, in which the metal manganese acts the part of a hexad element. Manganic acid itself has never been isolated. It is obtained, however, in combination with a few of the stronger metallic bases, forming manganates, of which the alkaline manganates only dissolve in water giving *green solutions.*

Manganates are readily decomposed in aqueous solution. On gently heating a solution of potassic manganate with free access of air, the green colour changes to *purple-red*, owing to the formation of potassic permanganate,* $Mn_2O_6(KO)_2 = \left\{\begin{matrix}'Mn^{v}O_2(OKO)\\'Mn^{v}O_2(OKO)\end{matrix}\right.$, and separation of hydrated dioxide thus :—

---

* Permanganic acid has never been isolated. It exists only in a few metallic salts called *permanganates*, some of which are soluble in water, forming

$$3MnO_2(KO)_2 + 3OH_2 = Mn_2O_6(KO)_2 + MnO(HO)_2 + 4KHO.$$

The change is accelerated by adding a few drops of a dilute mineral acid, *e.g.*, nitric, hydrochloric, or sulphuric acid, which combines with the liberated alkali. This reaction is extremely delicate.

The metal manganese seems to act here the part of a pseudo-octad element; and it may readily be inferred that the different oxygen atoms perform different functions in such a highly oxygenized compound, and that the metal manganese will part with some more readily than with others.

Manganic dioxide, as well as other native peroxides, already enumerated, also the alkaline manganates and permanganates, act as powerful oxidizers, differing merely in the *intensity* of their oxidizing action.

Manganic dioxide gives off oxygen on the addition of concentrated sulphuric acid, and forms normal manganous sulphate:—

$$MnO_2 + H_2SO_4 = O + MnSO_4 + OH_2.$$

Sulphuric acid added to sodic manganate, gives off a molecule of oxygen, and forms manganous and sodic sulphates, thus:—

$$Na_2Mn_2O_4 + 2SO_4H_2 = O_2 + SO_4Mn'' + SO_4Na_2 + 2OH_2.$$

Sulphuric acid added to a solution of potassic permanganate, liberates five atoms of oxygen, and leaves manganous and potassic sulphates in the solution, thus:—

$$\left\{\begin{matrix} MnO_2(OKO) \\ MnO_2(OHO) \end{matrix}\right. + 3SO_4H_2 = O_5 + 2SO_4Mn + SO_4K_2 + 3OH_2.$$

Hydrochloric acid acts likewise upon the higher oxides of manganese with evolution of chlorine and formation of metallic chlorides and water. The peroxides of manganese, especially the ***black oxide***, constitute the principal substances, used together with hydrochloric acid, or sodic chloride and oil of vitriol, for evolving chlorine in the laboratory and on a manufacturing scale.

No other mineral oxidizing agent is capable of yielding from one molecular group of elements five atoms of oxygen; and there are but few elementary substances which resist the oxidizing action of potassic permanganate. Hydrogen, freshly-ignited carbon, phosphorus, iodine, sulphuretted hydrogen, carbonic disulphide, are oxidized more or less rapidly. Metals, such as zinc and iron, become oxidized after a few days; lead, copper, mercury and silver, after some time. Many lower oxides, chlorides, etc., are converted into higher oxides, etc., especially in the presence of a free acid (hydrochloric or sulphuric acid).

Thus arsenious is converted into arsenic acid, sulphurous into sulphuric, nitrous into nitric, phosphorous into phosphoric acid. Oxalic acid is oxidized into carbonic anhydride and water. Lower

---

intensely purple-red solutions. The salts crystallize from an alkaline solution in beautiful large crystals of a deep violet lustre.

or -ous chlorides, sulphates, etc., are converted into the higher or -ic salts, *e.g.*, ferrous, stannous, antimonious, cuprous, and mercurous chlorides are oxidized ("chlorinized") in the presence of free hydrochloric acid into ferric, stannic, antimonic, cupric, and mercuric chlorides; the manganese and potassium of the permanganate are left in solution as chlorides. Ferrous, cuprous, and other sulphates are converted in the presence of free sulphuric or hydrochloric acid into ferric or cupric sulphates.

Potassic permanganate oxidizes also many organic bodies, such as sugar, gum, cellulose (in paper, cotton), uric acid, etc. The reaction in all these cases is indicated by a change of colour. On adding, for instance, the purple-coloured permanganate solution to a solution of sulphurous acid, the colour is instantaneously destroyed as long as any sulphurous acid is left. Permanganate becomes, therefore, the measure for sulphurous acid, and in like manner for other lower oxides, chlorides, etc.

Sulphurous acid requires one atom of oxygen in order to be converted into sulphuric acid, and potassic permanganate can part with five atoms of oxygen. One molecule of the oxidizing agent oxidizes, therefore, five molecules of the reducing agent, *i.e.*, 316 parts by weight of potassic permanganate become the measure for 5 × 64 = 320 parts by weight of SO_2.

Two molecules of ferrous sulphate combine with one atom of oxygen and one molecule of sulphuric acid, to form one molecule of ferric sulphate, thus:—

$$2FeSO_4 + O + SO_2(HO)_2 = S_3O_6Fe_2O_6 + OH_2, \text{ or } 2FeSO_4 + O + H_2SO_4 = Fe_2 3SO_4 + OH_2.$$

Hence one molecule of dipotassic permanganate oxidizes ten molecules of $FeSO_4$, ten molecules of FeO, or ten atoms of Fe; and 316 parts by weight of $Mn_2O_6(KO)_2$ become the measure for—

10 × 152 parts by weight of $FeSO_4$
or 10 × 72 „ FeO
or 10 × 56 „ Fe.

QUESTIONS AND EXERCISES.

1. Which are the most important manganese ores?
2. Explain the action of concentrated $SO_2(HO)_2$ upon MnO_2, $MnO_2(NaO)_2$ and $Mn_2O_6(KO)_2$; and express the changes by equations.
3. Translate into graphic formulæ the constitutional formulæ of *pyrolusite*, *braunite*, *hausmannite*, *manganite*, *psilomelane*, *wad*, *varvicite*, and *tephroite*.
4. Describe the most characteristic blowpipe reactions for manganese compounds.
5. How can Mn be separated from Ni and Co?
6. How is Mn separated from calcium or from potassium?
7. What change does a solution of dipotassic manganate undergo when heated in contact with air?
8. State why Mn is separated with difficulty from Fe^{iv} by means of AmCl and AmHO.

9. By precipitating 2·622 grms. of a manganous salt with sodic carbonate and ignition of the precipitate, 1·325 grm. of Mn_3O_4 is left; what is the percentage of manganese in the salt?
10. What is the action of dipotassic permanganate upon HCl, SH_2, SO_2 $\left\{\begin{matrix}COHO\\COHO\end{matrix}\right.$, Cu_2Cl_2, $FeCl_2$, $SnCl_2$? Express the changes by equations.
11. How much sulphurous anhydride by weight and by volume (at 0° C. and 760 mm. barometrical pressure) will be required to decolorise a solution containing ·500 gram of dipotassic permanganate?
12. ·125 grm. of dipotassic permanganate had to be added to a given quantity of an acid ($SO_2(HO)_2$), solution of SO_2FeO_2. Calculate how much metallic iron the solution contained.
13. 1·240 grm. of CO_2 was evolved when 1·780 grm. of *pyrolusite* was treated with moderately concentrated $SO_2(HO)_2$ and $\left\{\begin{matrix}COKO\\COKO\end{matrix}\right.$. What is the percentage of MnO_2 in the ore, and how much chlorine gas by weight and by volume can be evolved from 100 grms. of the ore when treated with HCl?

ZINC, Zn″.—Occurs in nature chiefly as SULPHIDE, or *zinc blende*, *black jack*, ZnS; as CARBONATE, or *calamine*, $ZnCO_3$; and as SILICATE, or *zinc glance*, *electric calamine*, $ZnSiO_4,OH_2$, *Willemite*, $ZnOSiO_3$; also as OXIDE—the only oxide known—in *red zinc ore*, ZnO.

The metal is extracted from its oxide by distillation with carbon, being volatile at a high temperature. It is of a decided blue tint of colour; highly crystalline, and somewhat brittle when cold, but becomes malleable when heated to about 120° C. Its atomic weight = 64·90; specific gravity = 7·15; melting point = 412° C.; boiling point, about 1040° C. It oxidizes superficially in air, and decomposes water slowly at the boiling point (100° C.), and rapidly at a red heat. It dissolves in most acids, displacing two equivalents of hydrogen.

REACTIONS IN THE DRY WAY.

The most characteristic blowpipe reaction for zinc consists in the white incrustation of zincic oxide which its compounds yield when heated on charcoal in the reducing flame with sodic carbonate. The zinc compound is reduced to the metallic state, and the metal being volatile, burns, on passing through the outer flame, with a bluish-green flame, and is converted into oxide, which covers the charcoal with an incrustation, **yellow** when hot, **white** when cold, and which assumes a **fine green** colour when treated with a solution of cobaltous nitrate, and on being once more strongly heated in the outer flame. The incrustation is not driven away in the oxidizing flame—zincic oxide being non-volatile.

Zinc compounds give with borax or microcosmic salt in both flames a bead, which is yellowish while hot, and white on cooling; opaque if much zinc salt be present. This applies, however, only to pure zinc compounds, and the detection of zinc by the blowpipe in poor ores containing other readily oxidizable metals (such as Pb

Cd, As, Sb, which give likewise incrustations) is a matter of great uncertainty.

Zincic sulphide (*zinc blende*), when roasted in a tube of hard glass, loses part of its sulphur in the form of sulphurous anhydride, and forms some zincic sulphate, $ZnSO_4$ (*white vitriol*), which may be extracted with water.

Calamine leaves on ignition zincic oxide.

REACTIONS IN THE WET WAY.

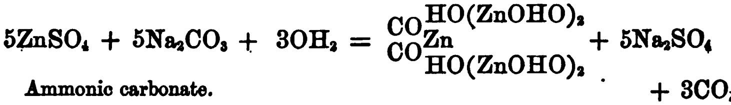
A SOLUTION of ZINCIC CHLORIDE, $ZnCl_2$, OR OF ZINCIC SULPHATE, SO_2ZnO'', $= SO_2(O_2Zn)''$, is employed. Both salts yield colourless solutions.

SAm_2 **(group reagent)** gives a *white* precipitate of **zincic sulphide**, ZnS, insoluble in excess. From dilute solutions the precipitate separates only after some time, more speedily in the presence of ammonic chloride. It is readily decomposed by dilute hydrochloric and sulphuric acids, with evolution of sulphuretted hydrogen; also by nitric acid, but is insoluble in acetic acid.

SH_2 precipitates zinc imperfectly from neutral solutions of zincic salts with mineral acids; but from an acetate or a solution of a zincic salt mixed with an alkaline acetate, the whole of the metal is precipitated by sulphuretted hydrogen as zincic sulphide, even in the presence of much acetic acid (METHOD OF SEPARATION OF Zn FROM Mn). Free organic acids prevent the precipitation.

KHO or $NaHO$ precipitates the *white* **hydrate**, $Zn(HO)_2$, readily soluble in excess, and in $AmHO$, reprecipitated almost entirely on diluting with water and on boiling, soluble also in ammonic chloride. Sulphuretted hydrogen precipitates the whole of the zinc from these solutions. Free organic acids prevent its complete precipitation. In the presence of the hydrates of manganese, nickel and cobalt, KHO or $NaHO$ does not dissolve out the whole of the zincic hydrate.

Sodic or potassic carbonate produces a *white* precipitate of **basic carbonate**, consisting of two molecules of zincic carbonate and three molecules of zincic hydrate, according to the equation:—



$$5ZnSO_4 + 5Na_2CO_3 + 3OH_2 = \begin{array}{ll} & HO(ZnOHO)_2 \\ CO & \\ & Zn \\ CO & \\ & HO(ZnOHO)_2 \end{array} + 5Na_2SO_4 + 3CO_2.$$

Ammonic carbonate.

Dihydric pentazincic dicarbonate tetrahydrate.

A large excess of ammonic salts prevents the precipitation.

This carbonate leaves on ignition ZnO, zincic oxide, also known under the name of *zinc white*.

Ammonic carbonate produces the same precipitate, soluble however, in excess.

KCy gives a *white* precipitate of **zincic cyanide**, $ZnCy_2$, soluble in excess, not reprecipitated by SAm_2, but completely precipitated by SK_2 as ZnS (Method for the separation of Zn from Ni).

Zinc precipitates the less electropositive metals from their solutions, viz., As, Sb, Sn, Cd, Cu, Pb, Ag, Bi, Hg: and on dissolving impure metallic zinc in dilute acids (hydrochloric or sulphuric), these metals do not dissolve, as long as any zinc remains undissolved. Hence zinc protects other metals, such as copper, iron (galvanized iron), &c., from the oxidizing action of the air and acids.

Zinc, when placed in contact with platinum, iron, &c., dissolves in alkaline solutions in the cold; when boiled with KHO (NaHO, or even AmHO), it dissolves likewise, with evolution of hydrogen and formation of **dipotassic zincic oxide**, $Zn(KO)_2$.

Zinc vapour decomposes CO_2 at a high temperature, and forms ZnO and CO; at a lower temperature, ZnO yields its oxygen again to carbon (Method of extracting metallic zinc from some of its ores). This forms an interesting instance of reciprocal chemical action.

QUESTIONS AND EXERCISES.

1. Explain the action of HCl, $SO_2(HO)_2$, HNO_3, and KHO upon metallic zinc. Express the changes by equations.
2. Give the names and composition of the most important zinc ores, and translate their constitutional into graphic formulæ.
3. Describe the blowpipe reactions for zinc compounds.
4. Express by equations the reactions for zinc in the wet way. Give graphic formulæ for the basic carbonate and dipotassic zincic oxide.
5. 1·5 grm. of *calamine* yielded ·876 grm. of ZnO, what is the percentage of zinc in the ore?
6. You have given to you *calamine*, *zinc blende*, hydrochloric acid, water, and sodic carbonate. State how you would prepare from these materials zincic oxide or *zinc white*. Express the changes by equations.
7. How is zinc separated from Mn, Ni, Co?

IRON. Fe$''$, ^{iv}, and ^{vi}.—One of the few metallic elements which occurs very abundantly in nature, mostly in a state of combination with oxygen and sulphur. It will suffice if those iron ores which contain the metal in sufficient quantities, and which are sufficiently free from deleterious substances (such as S, P, As), to render them suitable for the extraction of iron by the usual metallurgical processes, are considered. The most important are:—

1st. Ores containing Ferrous Oxide:—*spathic* or *sparry iron ore*, $FeCO_3$ (*sphaerosiderite*), containing varying quantities of $MnCO_3$, $MgCO_3$, and $CaCO_3$; *black band* or carbonaceous iron ore, a sphaerosiderite containing from 20 to 25 qer cent. of bituminous matter; *clay ironstone* (likewise a siderite) is, at its name indicates, associated with clayey matter. It is from these two ores that the greater part of the iron manufactured in this country is derived. They occur in immediate proximity to the coal measures and limestone beds—the fuel and flux necessary for their reduction to the metallic state.

2nd. ORES. CONTAINING FERROUS AND FERRIC OXIDES: *viz.*, *magnetic iron ore*, $Fe_3O_4 = \left\{\begin{matrix} FeO \\ FeO \end{matrix}\right. FeO_2$ (ferrous diferric tetroxide).

3rd. ORES CONTAINING FERROUS OXIDES ONLY: *viz.*, *red hæmatite* (*micaceous iron*, *oligist*, *specular iron*, or *iron glance*), $'Fe'''_2O_3 = \left\{\begin{matrix} FeO \\ FeO \end{matrix}\right. O$ (ferric oxide). This oxide forms different hydrates which, according to the amount of water which they contain, have received different names, *viz.*, *turgite*, $2Fe_2O_3,OH_2$ (tetraferric pentoxy-dihydrate); *needle iron ore*, *brown iron ore*, or *pyrrhosiderite*, $Fe_2O_3,OH_2 = \left\{\begin{matrix} FeOHO \\ FeOHO \end{matrix}\right.$ (diferric dioxy-dihydrate); *limonite* or compact *brown iron ore*, *brown hæmatite*, $2Fe_2O_3,3OH_2$ (tetraferric trioxy-hexahydrate); varieties: *oolitic iron ore*, *pea ore*); *yellow iron ore* or *xanthosiderite*, $Fe_2O_3,2OH_2$ (diferric oxy-tetrahydrate).

A few other iron ores deserve attention. They are not used for the extraction of iron, but are valuable as a cheap source of sulphur, viz., *iron pyrites*, *martial pyrites* or *mundic*, FeS_2, found abundantly in nature; Fe_2S_3 (diferric trisulphide); *copper pyrites*, Fe_2S_3,Cu_2S, and *magnetic pyrites*, $5FeS,Fe_2S_3 = Fe_7S_8$.

Besides these ores, iron is found in nature in combination with ARSENIC and SULPHUR, in *mispickel*, $\left\{\begin{matrix} ''As' \\ ''As' \end{matrix}\right. Fe,Fe^{iv}S_2$; with CHROMIUM as *chrome iron ore*, $FeOCr_2O_3$; with SILICA as *chloropal*, $\begin{matrix} SiO \urcorner \\ SiO = Fe_2O_6, \\ SiO \lrcorner \end{matrix}$ $3OH_2$, and many other silicates; as SULPHATE, in *green copperas* or *green vitriol*, $SO(HO)_2FeO_2,6OH_2$; as phosphate in *vivianite*,* $Fe_3P_2O_8,8OH_2$ (triferrous phosphate), and others; as ARSENATE, in *scorodite*, $Fe_2O_3As_2O_5,4OH_2$, and others.

All the oxides of iron part readily with their oxygen when heated with carbon. Metallic iron is silver-white on a fresh surface, which is very permanent in dry air, but rapidly changes, by oxidation, in moist air. Its atomic weight = 55·91. Specific gravity, 7·86. Melting point of iron is given by Pictet as 1600° C., by Carnelley as 1804° C. Varieties of iron, cast iron, steel, etc., melt at a much lower temperature; from 1050 to 1400° C. It decomposes water rapidly at a red heat, and readily displaces the hydrogen of strong mineral acids when in contact with water.

It combines directly with O, S, P, As and Cl, and forms alloys with nearly all other metals.

REACTIONS IN THE DRY WAY.

On heating the different iron compounds on charcoal before the blowpipe, they turn black and become magnetic; when heated in the *outer* flame, on a *borax* bead, iron compounds impart a **dark**

---

* Contains also ferric phosphate, $Fe_2P_2O_8.8OH_2$, to which the blue colour of the mineral is due.

red colour to the borax, whilst hot, becoming **light yellow**, when cold. In the *reducing* flame they give an **olive-green** to **bottle-green** bead.

The reactions with microcosmic salt are similar but less distinct. The presence of Co, Cu, Ni, Cr, conceals the colour of the iron bead. Ferric sulphides and arsenides must be roasted, previous to being introduced into the borax head. When heated with Na_2CO_3 on charcoal, in the reducing flame, metallic iron is obtained as a magnetic powder.

REACTIONS IN THE WET WAY.

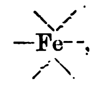
Iron forms two series of salts, viz., FERROUS AND FERRIC SALTS. It dissolves readily in dilute acids, such as HCl, $SO_2(OH)_2$, forming ferrous salts, $FeCl_2$, $FeSO_4$, with evolution of hydrogen. Cold dilute nitric acid dissolves finely divided iron (iron filings) without evolving hydrogen gas, the nitric acid being decomposed, so as to form ferrous nitrate and ammonic nitrate; the reaction may be expressed thus:—

$$4Fe + 10NO_2HO = 4Fe\begin{cases} NO_3 \\ NO_3 \end{cases} + NO_2AmO + 3OH_2.$$

The metal iron exists in all these salts in the dyad condition, but exhibits a marked tendency to pass into the tetrad condition. Exposed to the air, $FeCl_2$ and SO_4Fe absorb oxygen, and are gradually converted into ferric salts. The same change is produced by the action of various oxidizing agents, such as Cl, Br, I, ClNaO, KO_3Cl in the presence of HCl, NO_2HO, NO_2AgO, $AuCl_3$, $HgCl_2$, $Mn_2O_6(KO)_2$, $CrO_2(KO)_2$, and others. *Ferrous compounds are, therefore, powerful reducing agents.*

The tetrad condition appears to be the natural state of existence of the metal iron. This is rendered evident, moreover, by the limited number of ferrous compounds which exist in nature. The latter must be viewed as unsatisfied bodies, which, under favourable conditions, deprive other bodies, directly or indirectly, of oxygen, to form ferric compounds. Dyad iron, Fe'' (called *ferrosum*) has affinities latent, which it is eager to satisfy, so as to become converted into the more stable tetrad iron Fe^{iv} (or *ferricum*), in which condition it occurs in nature in combination with sulphur only, as FeS_2, without forming any corresponding oxygen, chlorine, etc., compounds. Two atoms of tetrad iron are invariably linked together in ferric oxide, chloride, etc., whereby iron becomes a pseudotriad element. It is possible to combine, by artificial means, three atoms of oxygen with one atom of iron, so as to form ferrates, as in potassic ferrate, $FeO_2(KO)_2$, in which compound the iron exists as a hexad element.

These different combining conditions of the metal iron may be represented graphically, thus:—

Dyad iron

Fe
e.g., in $FeCl_2$, FeO. FeS.

The precipitation is complete only in the presence of sodic or ammonic acetate, thus:—

$$Fe_2Cl_6 + 2Na_2HPO_4 + 2\left\{\begin{matrix}CH_3\\CONaO\end{matrix}\right. = P_2O_2Fe_2O_6 + 6NaCl + 2\left\{\begin{matrix}CH_3\\COHO\end{matrix}\right..$$

On the addition of the first few drops of hydric disodic phosphate, and as long as the ferric salt is largely in excess, the precipitate may disappear again, especially on gently warming, since it is somewhat soluble in ferric acetate. When the precipitation is nearly complete, the ferric phosphate separates more speedily, especially on stirring and gently heating, and allowing to subside after each addition of the phosphate solution. The precipitated ferric phosphate should be filtered hot, and washed by decantation with hot water. It is soluble in dilute mineral acids—hence the addition of an alkaline acetate; insoluble, however, in acetic acid, like the corresponding chromic* and aluminic phosphates.

Phosphates of the alkaline earthy metals (Ba, Sr, Ca, Mg), which are readily soluble in acetic acid, may thus be separated by filtration from the phosphates of Fe^{iv}, Al^{iv}, (and Cr^{iv}). Owing to this property of ferric phosphate, it is also possible to decompose alkaline earthy phosphates, in a sodic acetate and acetic acid solution, by adding, drop by drop, a neutral solution of ferric chloride, according to the equation:—

$$2BaHPO_4 + 2\left\{\begin{matrix}CH_3\\CONaO\end{matrix}\right. + \left\{\begin{matrix}CH_3\\COHO\end{matrix}\right. + Fe_2Cl_6 = P_2O_2Fe_2O_6 + 2BaCl_2 + 2NaCl + 3\left\{\begin{matrix}CH_3\\COHO\end{matrix}\right.,$$

as long as a yellowish-white precipitate comes down, and till the supernatant liquid becomes just red, from the formation of ferric acetate.

Ferric phosphate dissolves in excess of hydric disodic phosphate, in the presence of ammonic hydrate or carbonate, to a brownish-red solution. It is somewhat soluble in ferric, but not in ferrous acetate. Alkalies decompose it with difficulty only. Ammonic hydrate reduces it to a basic phosphate, $Fe_2P_4O_{19} + 16OH_2$ or $Fe_2P_4O_{19}16OH_2$. Potassic or sodic hydrate removes nearly the whole of the acid. Fusion with caustic fixed alkalies, or with fusion-mixture, or boiling with ammonic sulphide, decomposes ferric phosphate completely, leaving the iron as oxide or sulphide, from which the soluble alkaline phosphate can be separated readily by filtration.

Citric or tartaric acid prevents the precipitation of ferric phosphate.

K_4FeCy_6 gives a *fine blue* precipitate, $3FeCy_2,2Fe_2Cy_6$, known as

---

* Chromic phosphate, especially when freshly precipitated, is dissolved, although with some difficulty, in acetic acid, especially on heating.

Prussian blue, thus:—$2Fe_2Cl_6 + 3K_4FeCy_6 = 3FeCy_2,2Fe_2Cy_6 + 12KCl$. Insoluble in hydrochloric acid; decomposed by KHO or NaHO; soluble in oxalic acid; soluble also in excess of K_4FeCy_6, to a blue solution.

$K_6Fe_2Cy_{12}$ produces no precipitate, but the yellow colour of the ferric solution changes to *reddish-brown*. (Distinction between ferrous and ferric salts.)

CyAmS (**Ammonic sulphocyanate**) gives a *dark red* or *blood red* colour, even in the case of very dilute solutions, which is not destroyed by hydrochloric acid. The sensitiveness of the reaction is heightened by shaking a hydrochloric acid solution containing mere traces of a ferric salt with ether. The *blood red* **ferric sulphocyanate**, $Cy_6Fe_2S_6$, being soluble in ether, becomes thus concentrated into a small bulk of liquid. The colour of the liquid is readily destroyed by a solution of mercuric chloride (also by tartaric or phosphoric acid). (Distinction of Fe'' from Fe^{iv}.)

This confirmatory test should invariably be applied, because ferric acetate, when heated in presence of acetic acid, gives likewise a deep red coloration, which becomes lighter coloured on cooling.

Excess of **sodic acetate**, added to a solution of ferric salt, produces a deep red-coloured liquid, owing to the formation of ferric acetate. On diluting and boiling, the whole of the iron is precipitated as **basic ferric acetate** in the form of *brownish-yellow flakes*, which should be filtered hot, and as quickly as possible, as soon as the fluid has become clear. (Method for separating Fe^{iv} from Mn''.)

Ammonic succinate or **benzoate** precipitates ferric, but not ferrous salts, as **ferric succinate** or **benzoate**.* The ferric solution should be perfectly neutral. Salts of FeO, MnO, CoO, NiO, ZnO, are not precipitated. (Method of separation of Fe^{iv} from Fe'', Mn, Ni, Co, Zn.)

Freshly precipitated and well washed **baric** or **calcic carbonate**, suspended in water, precipitates ferric (not ferrous) chloride, as **ferric hydrate**, $Fe_2(HO)_6$, mixed with basic salt, with evolution of carbonic anhydride. The reagent is added to the *neutral* ferric salt *in the cold*, and well shaken up with it, till the *reddish-brown* precipitate acquires a whitish appearance, from excess of the alkaline earthy carbonate.

Barium carbonate separates in like manner the higher or -ic chlorides of this group from the lower or -ous chlorides. In order to separate ferric from ferrous compounds, or ferric chromic and aluminic compounds from ferrous, zincic, manganous, cobaltous, and nickelous salts, it is necessary that these metals should all be obtained in the form of chlorides, when, on the addition of baric carbonate, the respective hydrates, mixed with basic salts, are precipitated from the ferric, etc., chlorides, whilst ferrous chloride and the chlorides of Zn, Mn, Ni, and Co, are not affected. Air has to

---

* The formulæ of these compounds will be explained under the respective acids.

REACTIONS IN THE WET WAY.

Chromic salts can be prepared from the yellow $CrO_2(KO)_2 = K_2CrO_4$, or the red dipotassic dichromate, $K_2Cr_2O_7$, by heating with dilute hydrochloric acid and adding alcohol, when the yellow solution changes to a deep green solution of $Cr_2Cl_6 = \left\{\begin{array}{l} 'Cr'''Cl_3 \\ 'Cr'''Cl_3 \end{array}\right.$, in which the Cr exists as a tetrad or pseudotriad element.

Chromium is capable of forming three series of compounds*—

Chromous compounds containing dyad Cr.	Chromic compounds containing tetrad Cr.	Chromates containing hexad Cr.
$Cr''Cl_2$.	$'Cr'''_2Cl_6$.	CrO_3K_2O.
$Cr''O$.	$'Cr'''_2O_3$.	CrO_3PbO.
$Cr''(HO)_2$.	$'Cr'''_2(HO)_6$.	

of which only the two latter will be studied.

A. **Chromic Compounds.**—A solution of Chromic Chloride, Cr_2Cl_6, is employed.

SAm_2 (**group-reagent**) precipitates *bluish-green* **chromic hydrate,** $Cr_2(HO)_6$, insoluble in excess.

AmHO precipitates the **hydrate**, somewhat soluble in excess, the fluid acquiring a pink tint. The precipitation is complete on boiling.

KHO or NaHO, same precipitate, readily soluble in excess to a green solution: reprecipitated by long-continued boiling, or on adding AmCl, whereby the fixed alkali is removed as KCl or NaCl, with substitution of AmHO.

Sodic and potassic carbonates give *greenish* precipitates of **basic carbonates** (varying in composition), somewhat soluble in excess.

$POHO(NaO)_2$ (**hydric disodic phosphate**) precipitates *green* **chromic phosphate,** $P_2O_2Cr_2O_6 = P_2O_8Cr_2$, soluble in mineral acids, difficultly soluble in acetic acid.

Baric carbonate precipitates **basic carbonate.** The precipitation takes place in the cold, but is completed only after long digestion.

In the presence of citric, tartaric, and oxalic acid, and also of sugar, the precipitation of chromic salts by means of ammonia, sodic or baric carbonate, is more or less incomplete.

Chromic compounds may be recognized also by converting the chromic oxide into chromic acid. This may be accomplished:—

1st. By boiling a solution of Cr_2Cl_6 with PbO_2 and KHO or NaHO. The reaction which takes place, and which is indicated by a change of colour (from *green* to *yellow*), may be expressed thus:—

$$(1)\ Cr_2Cl_6 + 6KHO = \underset{\substack{\text{Soluble in} \\ \text{excess of KHO.}}}{Cr_2(HO)_6} + 6KCl.$$

---

* The intermediate oxides, Cr_2O_3CrO (chromous dichromic tetroxide), and CrO_2 (chromic dioxide) cannot be considered here. Possibly a lower oxide than CrO and a higher than CrO_3 exist, but have not been sufficiently studied.

$$(2)\ \mathrm{Cr_2(HO)_6 + 3PbO_2 = \underset{\substack{\text{Soluble in}\\ \text{KHO.}}}{2CrO_3PbO} + \underset{\substack{\text{Soluble in}\\ \text{KHO.}}}{PbO} + 3OH_2}.$$

On acidulating the solution with acetic acid a precipitate of plumbic chromate, $\mathrm{PbCrO_4} = \mathrm{CrO_2}\begin{smallmatrix}\cdot\mathrm{O}\\ \cdot\mathrm{O}\end{smallmatrix}\mathrm{Pb}$, is obtained.

2nd. By boiling a solution of Cr_2Cl_6 with NaHO and sodic hypochlorite, ClNaO, thus :—

$$\mathrm{Cr_2(HO)_6 + 3ClNaO + 4NaHO = \underset{\substack{\text{Yellow sodic}\\ \text{chromate.}}}{2Na_2CrO_4} + 3NaCl + 5OH_2}.$$

3rd. By fusion with alkaline carbonates and nitre (or, better still, with potassic chlorate) on platinum foil.

B. **Chromic anhydride**, $Cr^{vi}O_3$, combines with water to form chromic acid, CrO_3H_2O or H_2CrO_4. This forms with monad metals two classes of salts, the *normal* or *yellow chromates*, viz., $CrO_2(KO)_2$, and the *orange-red dichromate*, $\left\{\begin{array}{l}\mathrm{CrO_2KO}\\ \mathrm{O}\\ \mathrm{CrO_2KO}\end{array}\right.$, isomorphous with the corresponding sulphate and disulphate. A solution of the neutral (yellow) chromate is changed to an orange-red (acid) dichromate solution on boiling with nitric acid, one half of the alkaline base being removed in the form of potassic nitrate. The two salts are separated by crystallization. The dichromates appear to be combinations of CrO_3 with the normal chromates like K_2CrO_4. Higher chromates are also known, and may be easily obtained by treating an alkaline or other chromate with nitric acid, which removes some of the positive metal, leaving the higher chromium salt. They are generally less soluble than the normal salts, and more intensely coloured.

The anhydride may be prepared by slowly adding to a cold saturated solution of the red dipotassic dichromate 1½ times its bulk of concentrated sulphuric acid, and allowing it to cool slowly. CrO_3 crystallizes out in brilliant crimson-red prisms. The mother-liquor is poured off, and the crystals placed to drain upon a porous tile or slab of unglazed porcelain (biscuit), and kept covered with a bell-jar. They must be preserved in a well-stoppered bottle.

Chromic anhydride is one of the most powerful oxidizing agents known. Two molecules of CrO_3 yield upon ignition chromic oxide and three atoms of oxygen, according to the equation :—

$$2CrO_3 = Cr_2O_3 + O_3.$$

The metal chromium appears to exist in nature mostly in the tetrad and hexad state, as a glance at its natural compounds will show. Chromium differs, however, in a marked manner from iron and manganese, which can likewise exist in the tetrad and hexad state, by forming more stable hexad compounds (chromates), whilst in perchromic acid, on the other hand, the metal chromium appears to hold the oxygen less firmly than manganese holds it in permanganic acid.

REACTIONS OF CrO_3 BASED UPON ITS OXIDIZING ACTION.

A SOLUTION OF DIPOTASSIC DICHROMATE, $K_2CrO_4,CrO_3 = K_2Cr_2O_7$, may be employed.

SH_2, in the presence of free hydrochloric acid, reduces the orange-red solution to a green liquid, sulphur only being precipitated, thus:—

$$K_2Cr_2O_7 + 8HCl + 3SH_2 = Cr_2Cl_6 + 2KCl + 7OH_2 + S_3.$$

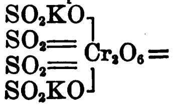
SAm_2, added in excess to a solution of an alkaline chromate or dichromate, precipitates *dirty green* **hydrated chromic chromate.** On boiling, the whole of the chromium separates as *green* **chromic hydrate,** thus:—

$$*K_2Cr_2O_7 + 3SAm_2 + 7OH_2 = Cr_2(HO)_6 + S_3 + 2KHO + 6AmHO.$$

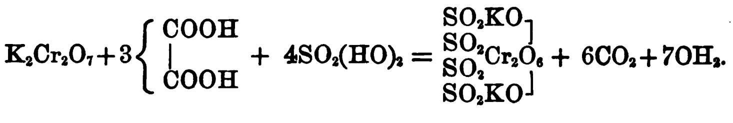
In the one case the H_2 of the SH_2 acted as the reducing agent; in the other the $(NH_4)_2$ of the SAm_2.

H_2SO_3, in the presence of a little free $SO_2(HO)_2$, reduces potassic dichromate to chromic sulphate, thus:—

$$K_2Cr_2O_7 + 3SO(HO)_2 + SO_2(HO)_2 = S_3O_6Cr_2O_6 + SO_2(KO)_2 + 4OH_2.$$

Chromic sulphate and potassic sulphate constitute potassium chrome alum, or (dipotassic chromic tetrasulphate)  $\left.\begin{array}{l}SO_2KO\\SO_2=\\SO_2=\\SO_2KO\end{array}\right] Cr_2O_6 =$ $K_2Cr_2S_4O_{16}$.

$\begin{array}{l}COOH\\|\\COOH\end{array}$ (**oxalic acid**), in the presence of free acid (dilute sulphuric acid), produces the same reaction, carbonic anhydride being evolved. Six molecules of CO_2 become the measure for one molecule of dipotassic dichromate. Tartaric and citric acid act in like manner.



$$K_2Cr_2O_7 + 3\left\{\begin{array}{l}COOH\\|\\COOH\end{array}\right. + 4SO_2(HO)_2 = \left.\begin{array}{l}SO_2KO\\SO_2\\SO_2\\SO_2KO\end{array}\right] Cr_2O_6 + 6CO_2 + 7OH_2.$$

Concentrated sulphuric acid reduces the dichromate, on the application of heat, with evolution of oxygen and formation of potassium chrome alum, thus:—

---

* The action is much more complex than here given, some of the S becoming oxidized to SO_3, which combines with the AmHO, forming Am_2SO_4. The amount of S oxidized is generally a third of that represented as liberated in the above equation.

$$\left\{\begin{array}{l}CrO_2,KO\\O\\CrO_2,KO\end{array}\right. + 4SO_2(HO)_2 = \left.\begin{array}{l}SO_2,KO\\SO_2\\SO_2\\SO_2,KO\end{array}\right]Cr_2O_6 + 4OH_2 + O_3.$$

HCl (concentrated) evolves chlorine, and the hydrogen combines with the three available atoms of oxygen in the dichromate, thus:—

$$\left\{\begin{array}{l}CrO_2KO\\O\\CrO_2KO\end{array}\right. + 14HCl = Cr_2Cl_6 + 2KCl + 7OH_2 + 3Cl_2.$$

As_2O_3 (in a hydrochloric acid solution) is converted into $AsO(HO)_3$, thus:—

$$\left\{\begin{array}{l}CrO_2KO\\O\\CrO_2KO\end{array}\right. + 3As(HO)_3 + 8HCl = Cr_2Cl_6 + 2KCl + 3AsO(HO) + 4OH_2.$$

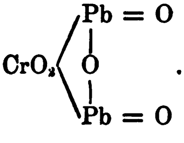
$SnCl_2$, $SbCl_3$, $FeCl_2$, Zn (Fe, Sn, etc.) in the presence of dilute HCl, reduce likewise chromates or dichromates. The reduction is effected also most readily by numerous organic bodies, such as alcohol in the presence of HCl, in which case the alcohol is oxidized to aldehyde, ethylic chloride, and other volatile products.

REACTIONS FOR CrO_3 PRODUCED BY DOUBLE DECOMPOSITION.

Chromates of the alkalies and alkaline earthy bases (with the exception of baric chromates), also of iron (Fe^{iv}), zinc, manganese, and copper, are soluble in water; all other chromates are insoluble, but dissolve readily in dilute nitric acid.

$BaCl_2$, added to a solution of a normal chromate (or dichromate), gives a *light lemon-yellow* precipitate of **baric chromate**, $BaCrO_4 = CrO_2{}^{O}_{O}Ba$, even in very dilute solutions; insoluble in acetic acid, difficultly soluble in *dilute* nitric or hydrochloric acid, and reprecipitated by AmHO.

$\left\{\begin{array}{l}CH_3\\CO\\CO\\CH_3\end{array}\right. Pb{}^{O}_{O}$ (**plumbic acetate**) gives a *fine lemon-yellow* precipitate of **plumbic chromate**, $PbCrO_4$, soluble in KHO, sparingly soluble in dilute nitric, insoluble in acetic acid. The neutral salt is converted upon digestion with alkalies into a basic red chromate,



$$CrO_5Pb_2 = PbCrO_4,PbO \text{ or } CrO_3\left\langle\begin{array}{l}Pb = O\\ \;\;|\\ \;\;O\\ \;\;|\\ Pb = O\end{array}\right. .$$

$AgNO_3$ (**argentic nitrate**) gives a *dark purple-red* precipitate of **argentic chromate**, CrO_4Ag_2, soluble in nitric acid and ammonia. From weak acid solutions **argentic dichromate**, $\left\{\begin{matrix}CrO_3Ag\\ O\\ CrO_3Ag\end{matrix}\right.$, is precipitated.

$Hg_2(NO_3)_2$ (**mercurous nitrate**) gives a *dark brick-red* basic precipitate of $Hg_2CrO_5 = HgCrO_4,HgO$, corresponding to the lead salt, which on ignition is converted into oxygen, mercury vapour, and finely divided green Cr_2O_3. (METHOD OF SEPARATING CHROMIC ACID FROM CHROMIC OXIDE.)

On bringing together a little chromic acid with hydric peroxide, O_2H_2, in an aqueous solution, a deep indigo-blue solution is produced, owing probably to the formation of PERCHROMIC ACID, in which compound chromium plays the part of a pseudo-octad element, analogous to manganese in permanganic acid.

A solution of perchromic acid decomposes, however, rapidly with evolution of oxygen, leaving $CrO_2(HO)_2$ and its constitution is yet doubtful. A solution in ether is far more stable than an aqueous solution. It is obtained by adding ether to a very dilute (acid) solution of O_2H_2, and then a drop of a dilute solution of a chromate. On shaking up gently, the ether takes up the whole of the perchromic acid, and acquires an intensely blue colour. Mere traces of CrO_3 can be discovered in this manner, or *vice versâ* the smallest quantities of O_2H_2.

QUESTIONS AND EXERCISES.

1. Which is the most important chromium ore? Give symbolic and graphic formulæ.
2. How is chromium detected in the dry way?
3. Describe how chromic chloride or sulphate is obtained from an alkaline chromate.
4. Describe the reactions by double decomposition which you can produce with chromic compounds. Give equations.
5. How can chromic compounds be converted in the wet way into chromates? Give instances, and express the changes by equations.
6. How is chromic anhydride prepared?
7. Give instances of the oxidizing action of chromic acid. Express the changes by symbolic equations.
8. You have given to you oxalic, hydrochloric, and concentrated sulphuric acids, dipotassic dichromate and water. State how you would prepare CO_2 or Cl gas from these materials, and express the changes by equations.
9. Describe some of the most characteristic reactions for chromic acid produced by double decomposition. Give equations.
10. How would you distinguish between chromic oxide and chromic acid occurring in one and the same solution?
11. Which chromates are soluble and which are insoluble in water?
12. How can Cr be separated from every other metal of Group III, except Mn?
13. How can Cr_2O_3 be separated from Fe'', Zn'', Mn'', Ni'', Co'' salts?
14. 1·600 grm. of *chrome iron ore* yielded 2·95 grms. of CrO_2PbO_2. What percentage of Cr does the ore contain?

15. 1·2 grm. of a sample of sodic chromate yielded with oxalic acid ·89 grm. of carbonic anhydride. What percentage of chromic anhydride did it contain?

ALUMINIUM, Al'' and ^{iv}.—One of the metallic elements which occur most abundantly in nature, both in the form of the OXIDE, and, as an important constituent of many minerals, in combination with SILICA, with SULPHURIC, PHOSPHORIC, and other acids; and in the form of FLUORIDE in *cryolite*, and the rare *topaz*. The element in the metallic state is not known free in nature, but is obtained by heating its chloride with sodium. It is white, with a decided blue tint, has about the hardness of copper, is very malleable and ductile, and is permanent in air. Water scarcely acts upon it, but diluted mineral acids dissolve it readily. Its atomic weight = 27·01; specific gravity = 2·60; melts at about 800° C., and is not volatile. It is an excellent conductor of heat and electricity, and forms alloys with most other metals.

REACTIONS IN THE DRY WAY.

Alumina, when heated on charcoal, is distinguished from other earths by its property of assuming a beautiful SKY-BLUE colour, after being moistened with a solution of cobaltous nitrate and ignited once more strongly, owing to its forming with the cobalt oxide a salt—cobaltous aluminate. This test is not always decisive, and becomes inapplicable when coloured oxides, such as Fe_2O_3, MnO, etc., are present, in which case recourse must be had to the tests for the element in solution in order to discover Al_2O_3.

REACTIONS IN THE WET WAY.

Soluble salts of aluminium, like the chloride Al_2Cl_6, or alum $= Al_23SO_4,K_2SO_424Aq = S_4O_8(KO)_2Al_2O_6,24OH_2$, may be used for testing.

SAm_2 gives a *white gelatinous* precipitate of **aluminic hydrate**, $Al_2(HO)_6$, sulphuretted hydrogen being evolved thus:—

$$S_4O_8(AmO)_2Al_2O_6 + 3SAm_2 + 6OH_2 = Al_2(HO)_6 + 4Am_2SO_4. + 3SH_2.$$

KHO or $NaHO$* precipitates the **hydrate**, readily soluble in excess, forming a saline compound, **Sodic Aluminate**, $Al_2Na_6O_6$, which is reprecipitated by excess of $AmCl$, or by $AmHO$ after neutralization of the alkali by hydrochloric acid. The alkaline solution is not precipitated by SAm_2 (Method of Separation of Al from Fe^{iv}).

---

* Potassic or sodic hydrate is mostly contaminated with alumina, derived during the manufacture from porcelain vessels, etc., and it is, therefore, absolutely necessary to employ pure NaHO (prepared in silver vessels) for the separation of Fe and Al. It must likewise be recollected that NaHO acts destructively upon porcelain and glass vessels; the precipitate should, therefore, not be heated longer than is necessary for its complete precipitation.

AmHO precipitates the **hydrate**, somewhat soluble in excess, insoluble in the presence of much ammonic chloride, and on boiling.

Sodic or potassic carbonate precipitates **basic carbonate** of uncertain composition.

Barium carbonate completely, but slowly, precipitates $Al_2(HO)_6$, even in the cold, mixed with **basic salt**. Carbonic anhydride escapes.

Hydric sodic phosphate gives a *bulky white* precipitate of **aluminic phosphate**, $Al_2P_2O_8$, insoluble in AmHO and AmCl; soluble in KHO or NaHO, like the hydrate (AmCl reprecipitates the phosphate from the soda solution), and in acids, but not in hot acetic acid (Distinction of Al_2O_3 from Aluminic Phosphate). Alkaline acetates precipitate $P_2O_2Al_2O_6$ from its solution in mineral acids. The presence of citric acid, but not of tartaric acid or of sugar, prevents its precipitation.

In order to decompose aluminic phosphate (*e.g.*, in the mineral *wavellite*, $P_4O(Al_2O_6)^{vi}{}_3 12OH_2$, it is best to fuse the finely powdered mineral with $1\frac{1}{2}$ part of finely divided SiO_2, and 6 parts of Na_2CO_3, in a platinum crucible for about half an hour. The mass is digested for some time with water, and COHOAmO added in excess; it is then filtered and washed. The residue consists of aluminic and sodic silicate, the solution contains the sodic phosphate. Dissolve the residue in dilute hydrochloric acid, and evaporate to dryness to separate the silicate and filter. The filtrate may be tested for Al in the usual way.

Alumina occurs mostly in minerals which are not soluble in acids. Boiling with concentrated sulphuric acid attacks many; all are, however, decomposed by fusion with SO_2HOKO, or $KHSO_4$, or with fusion mixture, and become readily soluble in water or in dilute hydrochloric acid.

Powder up some porcelain very finely, and fuse for half an hour in a platinum crucible, with four times its weight of fusion mixture. Extract with water. Transfer both the soluble and insoluble portion—consisting of alkaline aluminate—to a porcelain dish, acidulate with hydrochloric acid, and evaporate to dryness. Take up with a few drops of concentrated hydrochloric acid and hot water, and filter; wash the insoluble SiO_2 well with hot water. The filtrate contains the aluminium as Al_2Cl_6, from which it can be precipitated by ammonia as usual.

Aluminic silicate is often found in nature associated with potassic or sodic silicate, as in *felspar* (dipotassic aluminic hexasilicate), $Si_6O_8(KO)_2Al_2O_6$, and *albite*, $Si_6O_8(NaO)_2Al_2O_6$. In order to test for potassium and sodium, alkali salts must, of course, be carefully avoided. This can be done by making use of hydrofluoric acid.

Introduce a small quantity of finely powdered *felspar* into a platinum crucible or dish; treat with liquid hydrofluoric acid, and evaporate at a gentle heat in a closet or under a hood which is connected with the chimney. HF attacks the SiO_2, forming silicic fluoride, SiF_4—a volatile compound—and leaves the aluminium and potassium behind as fluorides readily soluble in dilute hydrochloric acid:—

$$Si_6O_8(KO)_2Al_2O_6 + 32HF = 6SiF_4 + 2KF + Al_2F_6 + 16OH_2.$$

The decomposition is generally only completed after two or three evaporations with HF.

QUESTIONS AND EXERCISES.

1. Enumerate some of the more important aluminium minerals; give constitutional and graphic formulæ.
2. How is Al_2O_3 detected in the dry way?
3. Give equations for the reactions of aluminium in the wet way.
4. How can insoluble aluminium minerals be rendered soluble in water or acids?
5. Explain the action of HF upon *felspar* and *albite*.
6. How can Al_2O_3 be separated from Fe_2O_3?
7. How is Al_2O_3 separated from Fe'', Zn'', Mn'', Ni'', Co'' in combination?
8. How can Al_2O_3 be distinguished from $P_2O_2Al_2O_6$.

The separation of the metals of Group III is surrounded by some difficulties, on account of the unavoidable complication which arises from the possible simultaneous precipitation of

1st. *Sulphides*, NiS, CoS, MnS, ZnS, FeS,
2nd. *Hydrates*, $Cr_2(HO)_6$, $Al_2(HO)_6$, and
3rd. *Phosphates* of Cr, Al, Ba, Sr, Ca, Mg,

and it is therefore well always to ascertain, by a special experiment, whether phosphoric acid, in combination with the above metals, is present or not in the solution under examination.

This can readily be done by adding AmCl, AmHO, and SAm_2 together to a small portion of a solution of metals of this group (or to the filtrate from Group II). On dissolving the precipitate which these reagents produce in a little concentrated nitric acid, and adding a solution of ammonic molybdate,* a yellow precipitate is obtained (especially on digesting for some time at a gentle heat), showing the presence of phosphoric acid. If no precipitate is obtained, the solution need only be examined for Ni, Co, Mn, Zn, Fe, Al, and Cr.

I. **Phosphoric acid is absent.**—This is sufficiently indicated if the original substance dissolved readily in water. If insoluble in water, but soluble in dilute acids, phosphoric acid may likewise be absent from the substance.

It would appear at first sight that the deportment of the five sulphides and two hydrates with ammonic chloride and ammonic hydrate, sodic or potassic hydrate, or dilute acids (*e.g.*, HCl), would enable the members of this group to be separated, or several of them, from each other. It has been seen, for example, that—

---

* For the preparation of this reagent see Appendix.

1st. *Ni, Co, Mn, Zn are not precipitated by AmHO from a hot solution containing large excess of AmCl; whilst* $Fe_2(HO)_6$, $Cr_2(HO)_6$, *and* $Al_2(HO)_6$ *are precipitated.* It has, however, been found that the mode of separation based upon this solvent property of ammonic chloride, gives but imperfect results, since the $Fe_2(HO)_6$ carries down varying quantities of other oxides, especially on exposure of the solution to the air, when higher oxides of manganese and cobalt are formed, which are not soluble in ammonic chloride. Small quantities of Ni, Co, Mn, and Zn are thus frequently overlooked altogether. It is only by redissolving the precipitate and reprecipitating several times over with AmCl and AmHO, as long as the ammoniacal filtrate gives a precipitate with sulphuretted hydrogen, that iron can be separated from manganese, etc., in this manner.

With these precautions, however, it is mostly possible to separate the metals of this group from each other by first precipitating ferric, chromic, and aluminic hydrates by means of AmCl and AmHO, and then from the filtrate, the sulphides of Ni, Co, Mn, and Zn by means of SH_2 or SAm_2; and the following method of separation may be consulted with advantage by beginners, as well as the more accurate, but more tedious one, of separation by barium carbonate (see Table, pp. 58 and 59).

2nd. *That Zn, Al, and Cr are precipitated by KHO or NaHO, but are soluble in excess, whilst the other metallic hydrates are insoluble.* From this it would appear that these three metals can be separated by means of the fixed alkaline hydrates. But it has been found that $Fe_2(HO)_6$, $Ni(HO)_2$, $Co(HO)_2$, $Mn(HO)_2$ carry down appreciable quantities of $Zn(HO)_2$ and more especially the $Fe_2(HO)_6$ precipitate of $Cr_2(HO)_6$, and that a complete separation cannot be effected by precipitation with KHO or NaHO.

3rd. *Cold dilute hydrochloric acid does not dissolve* CoS *or* NiS *to any great extent, but dissolves the other sulphides and hydrates.* This method, if practised with care, gives good results, small traces only of CoS and NiS being generally dissolved out. But as it leaves the iron, aluminium, and chromium still to be separated from manganese and zinc, no saving of labour is effected thereby in the separation of these seven metals.

Finely divided freshly precipitated **baric carbonate** *is a reagent which separates the lower oxides, viz.*, ZnO, MnO, NiO, CoO (this latter not quite so perfectly, except in the presence of much ammonic chloride), *from the higher oxides*, viz., Fe_2O_3, Al_2O_3, and Cr_2O_3. The metals should be first obtained as chlorides.

The examination of the *precipitate* produced by baric carbonate is based upon—

1st. The *solubility of* $Al_2(HO)_6$ *in NaHO.*

2nd. The *conversion of* Cr_2O_3 *into* CrO_3 *by fusion with sodic car-*

bonate and nitre, or by boiling with ClNaO, or with PbO_2 *in an alkaline solution.*

The examination of the *filtrate* is based upon—

1st. The *solubility* of $Zn(HO)_2$ *in sodic hydrate.*
2nd. „ MnS *in acetic acid.*
3rd. The *formation of soluble* $K_6Co_2Cy_{12}$ *and the precipitation of* Ni *as black* $Ni_2(HO)_6$ *by sodium hypochlorite,* ClNaO, *or chlorine or bromine.*

Directions for the separation of these seven metals will be found in the analytical tables under Group IIIA.

Tabulate the reactions produced by AmCl and AmHO, NaHO or SAm_2 with the members of Group IIIA, according to the following scheme:—

Reagent.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	ZnO.	MnO.	NiO.	CoO.
AmCl, and AmHO.	A *white gelatinous* precipitate of $Al_2(HO)_6$ slightly soluble in excess, re-precipitated on boiling.						
NaHO.	Ditto, soluble in excess.						
SAm_2.	A white gelatinous precipitate of $Al_2(HO)_6$, insoluble in excess.						

with the main view of fixing upon the memory the solubility or insolubility of the precipitates in excess of reagents.

II. **Phosphoric acid is present.**—The original substance was either insoluble or only partially soluble in water, but soluble in hydrochloric acid. In this case AmCl and AmHO* produce a precipitate before SAm_2 is added; the precipitate may possibly consist of NiS, CoS, MnS, ZnS, FeS, $Al_2(HO)_6$, $Cr_2(HO)_6$, as well as the phosphates of (Cr), Al, Mg, Ca, Sr, Ba.

It is obvious that ammonic phosphate is formed by the decomposition of the phosphates of the metals Ni, Co, Mn, Zn, Fe (if present) by SAm_2—AmCl and AmHO precipitate these phosphates without decomposition—which, in its turn, would act upon any soluble salts of Mg, Ba, Sr, Ca, and precipitate phosphates of these metals, although none may have been present originally in the

---

* If AmCl and AmHO should give no precipitate, it is obvious that no phosphates and no Fe, Al and Cr need be looked for.

SEPARATION OF THE METALS OF GROUP IIIA

Add AmCl in considerable excess; heat gently, and then add AmHO drop by
of Fe^{vi}.) Filter quickly, and wash with hot water. Reserve the ammonia-
filter. Collect the acid solution in another beaker, and repeat in like
produces any precipitate in the filtrate. Mix now the different am-

<table>
<tr><td colspan="4">Solution.—Pass a current of SH_2 through the solution, and filter off ZnS, MnS, NiS, CoS.* Wash off the filter, and redissolve the precipitate in dilute HCl, with the addition of a few small crystals of $\left\{\begin{matrix}OCl\\OKO\end{matrix}\right.$. Add NaHO in excess, boil, and filter.</td></tr>
<tr><td rowspan="3">The Solution may contain Zn, as $Zn(NaO)_2$. Add SH_2. White precipitate of ZnS.
Presence of Zn.</td><td colspan="3">The Precipitate may contain $Mn(HO)_2$, $Co(HO)_2$, and $Ni(HO)_2$. Wash, dissolve in a little dilute HCl; nearly neutralize with AmHO; add excess of $\left\{\begin{matrix}CH_3\\COONH_4\end{matrix}\right.$; pass a rapid current of SH_2 for several minutes through the solution and filter.</td></tr>
<tr><td rowspan="2">The Solution contains the manganese as acetate.
Add AmCl, AmHO and Sulphuretted Hydrogen Water.
Flesh-coloured precipitate of MnS.
Presence of Mn.</td><td colspan="2">Residue.—Dissolve in HCl and $KClO_3$; nearly neutralize with Na_2CO_3; add a weak solution of KCy, so as just to redissolve the precipitate first produced. Boil briskly for some time, allow to cool (filter off any slight precipitate), and add a <i>strong</i> solution of NaOCl†; allow to stand for some time in a warm place, as long as a black precipitate forms, and filter.</td></tr>
<tr><td>Precipitate consists of $Ni_2(HO)_6$. Filter off and confirm by heating a small portion of it on a borax bead before the blowpipe flame.
A yellowish to sherry-red bead.
Presence of Ni.</td><td>The Solution contains the cobalt as $K_6Co_2Cy_{12}$. Evaporate to dryness, and test a little of the residue before the blowpipe flame on a borax bead.
A blue bead in both flames.
Presence of Co.</td></tr>
</table>

---

* Unless this precipitate is black no Ni nor Co need be looked for, if

† Strong bromine water or a few bubbles of chlorine gas act better than

BY MEANS OF AmCl, AmHO, AND SAm₂.

drop as long as a precipitate comes down. (The iron must be present in the form cal filtrate. Redissolve the precipitate by treating it with hot dilute HCl on the manner the precipitation with AmCl and AmHO as long as good SH_2 water moniacal filtrates with the main filtrate.

The **Precipitate** consists of $Fe_2(HO)_6$, $Cr_2(HO)_6$, and $Al_2(HO)_6$. Dissolve in dilute HCl, add a solution of NaHO (free from alumina) in excess, and boil for some time. Filter off.

Precipitate.—Dry and fuse, with fusion mixture and nitre on platinum foil. Dissolve in hot water, and filter.

Residue.—Dissolve in dilute HCl, and add K_4FeCy_6.
A precipitate of Prussian blue.

Presence of Fe.

Test the original HCl solution specially for ferrous and ferric iron by means of potassic permanganate in a highly dilute solution as well as by means of K_4FeCy_6, $K_6Fe_2Cy_{12}$, or AmSCN.

Solution, yellow. Confirm by adding $\left\{\begin{matrix} CH_3 \\ COHO \end{matrix}\right.$ and $\left(\left\{\begin{matrix} CH_3O_2 \\ CH_3O_2 \end{matrix}\right.Pb\right)$.
Yellow precipitate of $PbCrO_4$.

Presence of Cr.

Note.—Traces of manganese—owing to imperfect separation of Mn from Fe by precipitation with AmCl and AmHO—are indicated by the *bluish-green* colour of the fused mass arising from the formation of an alkaline manganate, and after dissolving in water, by the *purplish-red* colour of the alkaline permanganate.

Solution. — Acidulate with dilute HCl, and add AmHO in *slight* excess.
White gelatinous precipitate.

Presence of Al.

Note.—If no sodic hydrate free from alumina can be obtained, it is necessary to test an equal bulk of the reagent by acidulating with HCl and adding a *slight* excess of AmHO, and then comparing the $Al_2(HO)_6$ thus precipitated with the precipitate obtained in testing the solution under examination.

---

black, the four may be present.
NaOCl.

saline mixture. An example will make this clear. Supposing that the substance under examination consists of barium carbonate and calcium and ferric phosphates, $CO_3Ba, P_2O_8Ca_3$ and $P_2O_8Fe_2$. On dissolving in hydrochloric acid, baric chloride is formed, and the calcic and ferric phosphates are dissolved without decomposition. On adding AmCl and AmHO, a yellowish-white precipitate of $P_2O_8Fe_2$ and $P_2O_8Ca_3$ is obtained, whilst $BaCl_2$ is not precipitated. On adding, however, SAm_2 as well as the AmCl and AmHO to the solution, $P_2O_8Fe_2$ is decomposed into ferrous sulphide and ammonic phosphate, which latter, by acting upon the $BaCl_2$, would precipitate baric phosphate.

In order to avoid this, the precipitate produced in Group III by AmCl and AmHO, which contains for the most part the whole of the phosphates, is filtered off and SAm added to the filtrate only. The two precipitates are washed separately, transferred to a porcelain dish, and boiled with a little SAm_2, which decomposes the metallic phosphates (possibly also some $Fe_2(HO)_6$), leaving the phosphates of the earths and alkaline earthy bases (if any), as well as the hydrates of Cr and Al, unchanged. The insoluble residue is filtered off and washed with hot water (to which a little SAm_2 has been added to prevent the oxidation of FeS, etc.); the filtrate is tested for phosphoric acid by means of AmCl, AmHO, and $MgSO_4$. A white crystalline precipitate shows that phosphoric acid was present, *in combination with the metals precipitable as sulphides.*

The residue is dissolved in a small quantity of hot hydrochloric acid, with the addition of a little concentrated nitric acid; filtered, if necessary, from the sulphur which separates, and concentrated to a small bulk by evaporation. To a small portion of the solution add a little more concentrated nitric acid, and then some ammonic molybdate, and heat gently. In the absence of a yellow precipitate, no phosphates of (Cr), Al, Ba, Sr, Ca, Mg need be looked for, and the solution may be examined at once according to Table IIIA. A yellow precipitate indicates *that phosphates of the earths or alkaline earthy bases*, or of both, are present, in addition to the metallic phosphates already tested for.

If so, add sodium carbonate to the rest of the solution till nearly neutral, then an excess of a solution* containing sodic acetate and strong acetic acid: ferric phosphate, $Fe_2P_2O_8 = P_2O_2Fe_2O_6$ (as well as $P_2O_2Cr_2O_6$ and $P_2O_2Al_2O_6$ if present), is precipitated. Any phosphates of the alkaline earths left undecomposed by the ferric chloride already present in the solution, are held in solution by the acetic acid. To the filtrate add Fe_2Cl_6, drop by drop, as long as a precipitate† is obtained, and till the colour of the supernatant liquid becomes distinctly reddish. Digest at a gentle heat: allow to subside and filter. In this manner the whole of the phosphates of the alkaline earthy bases are decomposed, with formation of P_2O_5,Fe_2O_3, insoluble in acetic acid—(which precipitate may be neglected), and chlorides of Mg, Ba, Sr, Ca which remain in solution, together with the chlorides of Ni, Co, Mn, Zn (and the excess of Fe_2Cl_6 added). The whole of the phosphoric acid having thus been removed, the precipitate produced by AmCl, AmHO and SAm_2 is examined according to Table IIIA. The alkaline earthy metals are separated according to Tables IV and V. It should be borne in mind that these metals can have been present in the original substances only as phosphates, and the filtrate which contains them should on no account be mixed up with the main filtrate from Group III, but should be examined separately.

---

* For the preparation of this reagent see Appendix.

† If any phosphates of the alkaline earthy bases be left, Fe_2Cl_6 should produce a yellowish-white precipitate when added to *a portion of the acetic acid solution*; if not, no ferric salt need be added to the *main portion of the filtrate.* (The presence of iron, other than phosphate, is generally indicated by the reddish or ferric acetate colour of the filtrate.) In this case Al and Cr, as well as the metals of the alkaline earths, will still have to be looked for in the filtrate.

It may be of interest to ascertain whether oxalates of Ba, Sr and Ca (which are destroyed by evaporation with nitric acid and ignition, before proceeding to Group III), were present in the original mixture, in which case the evaporation to dryness and ignition must be omitted.

The precipitate produced in Group III by AmCl and AmHO alone contains the oxalates, as well as the phosphates of the alkaline earthy bases, and possibly also gelatinous silica. The oxalates are decomposed by gently igniting the precipitate, and are converted into carbonates. The ignited mass effervesces strongly on extracting with dilute hydrochloric acid. When the solution is evaporated to dryness and again taken up with dilute HCl, the silica, if present, is rendered insoluble, and may be separated by filtration. To the acid solution, which may possibly contain phosphates of Mg, Ca, Sr, and Ba, as well as chlorides of the bases, present before ignition as oxalates, add AmCl and AmHO and filter off. The filtrate contains the chlorides of Ba, Sr and Ca, and is tested separately according to Table IV. ALL BASES SO DISCOVERED MUST HAVE BEEN PRESENT ORIGINALLY AS OXALATES.

THE SEPARATION OF THE METALS AND SALTS (PHOSPHATES) PRECIPITATED IN GROUP IIIB is based upon :—

1st. *The insolubility of the phosphates of Fe, Al (and Cr) in acetic acid in the presence of an alkaline acetate.*

2nd. *The separation of the whole of the phosphoric acid which is in combination with the alkaline earthy bases, by means of* Fe_2Cl_6, *in an acetic solution.*

All other operations are identical with those described in Tables IIIA, IV and V.

A tabular scheme for their examination* will be found in the analytical tables, under Group IIIB.

---

* The examination of Group IIIB, containing phosphates, may be deferred until the student has become acquainted with the reactions for acids.

QUESTIONS ON GROUP IIIB.

1. How would you recognize alumina in the presence of aluminic phosphate?
2. Given a reddish coloured solution (owing to the presence of ferric salts), which gives a copious precipitate on the addition of sodic acetate and acetic acid in the cold, leaving the solution still coloured. What inference is to be drawn from this observation?
3. A solution contains chromic chloride, chromic phosphate, and dipotassic dichromate. State how you would distinguish these three chromium compounds from each other.
4. An acid solution (HCl) of a mixture, consisting of ferric chloride, baric chloride, and common sodic phosphate, retains its reddish colour, after precipitation with sodic acetate and acetic acid. What inference must be drawn from this, and what would you infer if the filtrate were colourless, but gave no further precipitate on the addition of Fe_2Cl_6?
5. You have a solution given to you which gives a precipitate with AmCl and AmHO. What inference must you draw if the filtrate gives no further precipitate on the addition of SAm_2?
6. You have given to you a concentrated solution of ferric chloride. On adding a few drops of a solution of hydric disodic phosphate, a yellowish precipitate appears. Explain what takes place, 1st. When a portion of the solution in which the precipitate is suspended is boiled. 2nd. When acetic acid is added, in the cold, to another portion. 3rd. When the precipitate is filtered and treated with excess of hydric disodic phosphate in the presence of ammonia.

CHAPTER V.

REACTIONS OF THE METALS OF GROUP II.

THIS group comprises the metals MERCURY, LEAD, BISMUTH, COPPER, CADMIUM, ARSENIC, ANTIMONY, TIN (GOLD AND PLATINUM), which are precipitated from acid solutions (HCl) by means of sulphuretted hydrogen.

Mix together solutions of $Bi_3(NO_3)_3$, $HgCl_2$, $CuSO_4$, $CdCl_2$, As_2O_3 (dissolved in HCl), $Pb(NO_3)_2$, $SbCl_3$, $SnCl_2$, and $SnCl_4$, and pass a current of SH_2, without first filtering off the white precipitate which is produced. Filter; pass the gas again through the clear filtrate, to make sure that the metals have been entirely precipitated. Wash the precipitate with hot water; remove a portion from the filter; boil with a little yellow ammonic sulphide, and filter off. A black residue is left, consisting of HgS, PbS, Bi_2S_3, CuS, CdS. The solution contains As_2S_3, Sb_2S_3, SnS and SnS_2. This can be shown by acidulating with dilute hydrochloric acid; when a yellow precipitate comes down—because yellow ammonic sulphide converts SnS into SnS_2,—consisting of the sulphides of As, Sb, Sn.

This shows that *Group II may be divided, by means of ammonic sulphide, into two portions.*

The name *sulphide*, in its widest sense, is given to all compounds into which sulphur enters as the electronegative element. A remarkable analogy is observable between oxides and sulphides. There is a certain class of sulphides which resembles metallic oxides or bases; another class which plays the part of oxy-acids. Sulphides are therefore divided into *sulpho-bases* and *sulpho-acids.* To the latter belong the sulphides of H, As, Sn, Sb (Pt, Au); to the former the sulphides of many metals, especially such of the metals as constitute powerful bases (K, Na, Am, Ba, Ca, etc.). An electropositive element, which forms with oxygen an oxide, combines generally also with the same number of sulphur atoms, to form a corresponding *sulphide*, in which the sulphur is performing similar functions to oxygen.

The resemblance in the constitution ot these oxygen and sulphur compounds is further borne out by the analogy in their solubility and alkaline reaction:—

Oxy-bases.			*Sulpho-bases.*		
OK_2	Potassic oxide,	alkaline and soluble.	SK_2	Potassic sulphide,	alkaline and soluble.
OAm_2	Ammonic oxide	„	SAm_2	Ammonic „	„
ONa_2	Sodic „	„	SNa_2	Sodic „	„
BaO	Baric „	„	BaS	Baric „	„
CaO	Calcic „	„	CaS	Calcic „	„
FeO	Ferrous oxide,	no reaction, insoluble.	FeS	Ferrous „	no reaction, insoluble.
ZnO	Zincic „	„	ZnS	Zincic „	„

Oxy-anhydrides.		*Sulpho-anhydrides.*	
As_2O_3	Arsenious anhydride.	As_2S_3	Arsenious sulphide, or sulpharsenious anhydride.
As_2O_5	Arsenic ,,	As_2O_5	Arsenic sulphide, or sulpharsenic anhydride.
Sb_2O_3	Antimonious ,,	Sb_2S_3	Antimonious sulphide, or sulphantimonious anhydride.
Sb_2O_5	Antimonic ,,	Sb_2S_5	Antimonic sulphide, or sulphantimonic anhydride.
SnO_2	Stannic ,,	SnS_2	Stannic sulphide, or sulphostannic anhydride.

Oxy-acids.		*Sulpho-acids.*	
$As(HO)_3$	Arsenious acid.	$As(HS)_3$	Sulpharsenious acid.
$AsO(HO)_3$	Arsenic acid.	$AsS(HS)_3$	Sulpharsenic acid.
$Sb(HO)_3$	Antimonious acid.	$Sb(HS)_3$	Sulphantimonious acid.
$SbO(HO)_3$	Antimonic acid.	$SbS(HS)_3$	Sulphantimonic acid.
$SbO_2(HO)$	Metantimonic acid.	$SbS_2(HS)$	Sulphometantimonic acid.
$Sn(HO)_4$	Stannic acid.	$Sn(HS)_4$	Sulphostannic acid.

Sulpho-salts are obtained by the mutual action of a sulpho-acid and a sulpho-base upon each other.

Sulphides soluble in water, comprising the sulphides of the alkalies and alkaline earthy metals, are divided into *normal sulphides*, such as SK_2, SAm_2, SNa_2, BaS; into *sulphydrates* (acid sulphides), such as SKH, SAmH, BaH_2S_2; and *polysulphides*, such as S_2H_2,S_5K_2, S_5Am_2. The aqueous solutions of the normal and acid sulphides are colourless, and give off SH_2, when treated with dilute hydrochloric acid, *without separation of sulphur*. Solutions of the polysulphides are yellow, or yellowish-brown, and when treated with hydrochloric acid, give off sulphuretted hydrogen, with separation of white (or precipitated) sulphur. The number of sulpho-salts is small compared with the salts of oxy-acids, and they are far less stable than ordinary oxy-salts. This arises from the fact that sulphur is comparatively indifferent to chlorine, phosphorus, nitrogen, carbon, silicon—non-metallic elements, which are endowed with a powerful chemical affinity for oxygen, with which they form in the presence of water energetic oxy-acids—and that there are either no sulphides corresponding to the oxygen compounds of these elements, or sulphides of a very indifferent nature. The number of sulpho-acids is principally restricted to the acids enumerated above, and these again combine mostly only with the soluble sulphides possessed of an *alkaline reaction;* or, if combined with the sulphides of the heavy metals, as in certain metals, they are readily decomposed by chemical agencies.

The following is a list of some of the more important sulpho-salts compared with the corresponding oxy-salts:—

Oxy-salts.		*Sulpho-salts.*	
$Sn(NaO)_2$	Disodic stannite.	$Sn(NaS)_2$	Disulphosodic sulphostannite.
$SnO(NaO)_2$	Disodic stannate.	$SnS(NaS)_2$	Disulphosodic sulphostannate.
$As(KO)_3$	Tripotassic arsenite.	$As(KS)_3$	Trisulphopotassic sulpharsenite.
$AsO(NaO)_3$	Trisodic arsenate.	$AsS(NaS)_3$	Trisulphosodic sulpharsenate.
$SbOKO$	Potassic metantimonite.	$SbSKS$	Sulphopotassic metasulphantimonite.
SbO_2KO	Potassic metantimonate.	SbS_2KS	Sulphopotassic metasulphantimonate.

In these sulphur compounds the supposed or hypothetical radical NaS, sodiumsulphyl, occupies the place of, or performs similar functions to the compound radical NaO, sodoxyl. In like manner

(KS)	Potassiumsulphyl	occupies the place of	(KO)	Potassoxyl.
(AmS)	Ammoniumsulphyl	„	(AmO)	Ammonoxyl.
BaS''	Bariumsulphyl	„	BaO''	Baroxyl.
CaS''	Calciumsulphyl	„	CaO''	Calciumoxyl,

in the analogous sulpho-salts.

Instances of some interesting natural sulpho-salts, to be considered more fully under silver and lead, are:—

$As(AgS)_3$, trisulphargentic sulpharsenite (*proustite*).

$Sb(AgS)_3$, trisulphargentic orthosulphantimonite (*pyrargyrite* or *dark red silver ore*).

$Sb_2S''(Cu_2FeS''_3)''_2$, sulphocuproso ferrous pyrosulphantimonite (*fahl ore*).

$Sb_2S_3(PbS)_3$, trisulphoplumbic orthosulphantimonite (*boulangerite*).

$4PbS.(Sb_2S_3)(Cu_2S)_2Sb_2S_3$, disulphoplumbic sulphocuprous orthosulphantimonite (*bournonite*).

$(PbS)_3(Sb_2S_3)_2$, trisulphoplumbic metasulphantimonite* (*jamesonite*). These minerals are seldom found of this composition, being generally more or less mixed with other minerals.

Treat another portion of the above SH_2 precipitate with NaHO or KHO and filter off. A black residue is likewise left, and on adding dilute HCl to the filtrate, As_2S_3, Sb_2S_3, SnS, and SnS_2 are reprecipitated.

This shows that the *hydrates of the alkali metals dissolve a portion of the sulphides precipitated by SH_2 in Group II.* The following equations explain the action of the alkaline hydrates:—

$$Sb_2S_3 + 6KHO = Sb(KS)_3 + Sb(KO)_3 + 3OH_2.$$

Antimonious sulphide.	Trisulphopotassic sulphantimonite.	Tripotassic antimonite.

$$As_2S_3 + 4KHO = AsHS(KS)_2 + AsHO(KO)_2 + OH_2.$$

Arsenious sulphide.	Sulphydric disulphopotassic sulpharsenite.	Hydric dipotassic arsenite.

---

* This compound may also be viewed as Sb_2S_2Pb'' (sulphoplumbic metasulphantimonite) and $Sb_2SPbS''_2$ (sulphoplumbic pyrosulphantimonite).

$$\underset{\text{Stannous sulphide.}}{2SnS} + 4KHO = \underset{\text{Disulphopotassic sulphostannite.}}{Sn(KS)_2} + \underset{\text{Dipotassic stannite.}}{SnO(KO)_2} + 2OH_2.$$

$$\underset{\text{Stannic sulphide.}}{2SnS_2} + 4NaHO = \underset{\text{Disulphosodic sulphostannate.}}{SnS(NaS)_2} + \underset{\text{Disodic stannate.}}{SnO(NaO)_2} + OH_2 + SH_2.^{*}$$

Addition of hydrochloric acid reprecipitates the sulphides, thus :—

$$SbKS_3 + Sb(KO)_3 + 6HCl = Sb_2S_3 + 6KCl + 3OH_2.$$

Hence the metals which are precipitated by SH_2 in Group II can be subdivided by means of SAm_2 or NaHO into—

A. *Metals whose sulphides act as sulpho-bases*, viz., the sulphides of Hg, Pb, Bi, Cu, and Cd. These are insoluble in ammonic sulphide (HgS dissolves to some extent in potassic or sodic sulphide ; CuS is somewhat soluble in ammonic sulphide).

B. *Metals whose sulphides act as sulpho-acids*, viz., the sulphides of As, Sb, Sn (Au, Pt).

GROUP II. SUBDIVISION A.

1. Mercury. Hg$''$.—Occurs native, but is chiefly obtained from *cinnabar* or mercuric sulphide, HgS, by heating with lime or iron turnings in a distilling apparatus or retort. The element is liquid at ordinary temperatures and down to about −40° C., at which temperature it crystallises. Both the solid and liquid states exhibit a metalline lustre and colour like silver. It has an atomic weight of 199·71, generally taken as 200. Specific gravity = 13·55 in the liquid and 14·19 in the solid state. The solid melts at −38·50° C. and boils at 357·25° C. under a pressure of 760 mm. It does not tarnish appreciably in the air, but is very slowly oxidized when gently heated, about 300° C., in an atmosphere of oxygen. Ozone acts more rapidly. Nitric acid acts readily upon it, even when cold. Sulphuric only when heated. Hydrochloric or alkalies have no action. It combines energetically with chlorine, bromine, iodine, and sulphur, also with sodium and potassium and most other metals, excepting iron and platinum forming amalgams

EXAMINATION IN THE DRY WAY.

Add a little finely-divided lead or zinc to a few globules of mercury on a watch-glass. The liquid metal mercury becomes thick and pasty by the combination with the solid metal lead or zinc. It enters into combination with the lead, in the cold, to form an *amalgam*. Some metals combine with mercury only when heated.

---

* No SH_2 is given off in this reaction. As excess of NaHO is always used, it may be represented :—

$$2SnS_2 + 5NaHO = SnS(NaS)_2 + SnO(NaO)_2 + 2OH_2 + NaHS.$$

The term amalgam is applied to the combinations into which mercury enters with other metals. Combinations between metals, other than mercury, are called *alloys*. This property of mercury has received an important application in the extraction of gold and silver from poor ores by the so-called *amalgamation process*, in which mercury can be separated again by distillation, gold and silver being left behind.

The combination of the metal mercury with other metals at the ordinary temperature is probably due to its liquid condition, which facilitates its being brought into intimate or molecular contact with other metals. This contact action is materially increased, if the solid metals are offered to the mercury in a finely divided condition, or in the form of foil. An amalgam of 4 parts of tin and 1 part of mercury is employed for making looking-glasses.

HgS (as well as SAg_2, Au_2S_3, PtS_2) parts with its sulphur when roasted in the air, and yields the metal; *it is in fact reduced to the metallic state by oxygen*, owing to the weak affinity which exists between the metal mercury and the non-metal sulphur, and owing likewise to its weak affinity for oxygen, on account of which the HgO (and OAg_2) first formed gives up its oxygen again to a fresh quantity of HgS (or SAg_2).

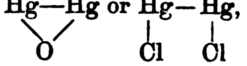
Hydrogen and carbon, copper, tin, zinc, etc., reduce HgS at a high temperature, forming with the sulphur SH_2, CS_2 (carbon disulphide), CuS, etc. The native HgS is, however, best reduced by the action of strong bases, such as lime or soda.

Mix a little cinnabar with dry sodium carbonate, and heat in a little tube, sealed up at one end, or blown into a small bulb. Metallic mercury sublimes and forms a mirror in the cold part of the tube; the sulphur is fixed by the alkali metal.

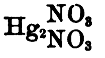
Mercury salts, when heated by themselves, out of contact with the air, **volatilize** or **sublime**, either without decomposition, such as $HgBr_2$, $HgCl_2$, Hg_2Cl_2 (without undergoing previous fusion), HgI_2,HgS ; or they are decomposed into oxide or metal. Salts of mercury with fixed acids (P_2O_5, CrO_3, etc.), leave fixed residues of acid or oxide (Cr_2O_3).

REACTIONS IN THE WET WAY.

Mercury forms two series of salts : **mercurous and mercuric salts.**

In mercurous salts the element exhibits less extent of energy of combination than in mercuric salts. As for instance in mercurous oxide, Hg_2O; calomel, Hg_2Cl_2; and mercuric oxide, HgO, corrosive sublimate, $HgCl_2$. In the former case it is supposed that the metal is in some way combined with itself as  $\underset{\diagdown O \diagup}{Hg—Hg}$ or $\underset{Cl\quad Cl}{Hg—Hg}$, whilst in the latter the whole of the energy of the mercury-atom is expended on the substance with which it is combined, $Hg=O$ or $HgCl_2$.

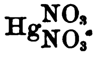
It dissolves readily in nitric acid, even in the cold, forming mercurous nitrate, if the mercury be in excess, and mercuric nitrate, if the acid be in excess. These salts have the composition—



$$Hg_2{}^{NO_3}_{NO_3}$$

Mercurous nitrate.

and



$$Hg^{NO_3}_{NO_3}.$$

Mercuric nitrate.

Mercurous oxide exhibits a tendency to combine with another atom of oxygen, or when exposed to heat, to part with one atom of mercury, and to become converted into mercuric oxide. Hence mercurous salts are powerful *reducing* agents.

On account of the *insoluble chloride* which $'Hg'_2$ forms, its reactions will be considered in connection with the reactions for silver and lead in Group I.

In order to study the reactions of mercuric salts, A SOLUTION OF MERCURIC NITRATE, $Hg(NO_3)_2$, or MERCURIC CHLORIDE, $HgCl_2$ (*corrosive sublimate*), may be employed.

SH_2 (**group-reagent**) added to $HgCl_2$ gives a *black* precipitate of **mercuric sulphide**, HgS. The precipitation is marked by characteristic changes of colour. Accordingly as sulphuretted hydrogen water is added in small quantities, or the gas passed slowly through the solution, it produces at first a perfectly *white* precipitate, and on the addition of more SH_2, a *yellow* precipitate which passes through *dirty yellow* to *brown*, and becomes *black* only when excess of SH_2 has been added to the mercuric salt. The white, yellow, or brown precipitate consists of varying quantities of HgS and $HgCl_2$. HgS is insoluble in nitric or hydrochloric acid and in yellow ammonic sulphide, potassic hydrate, or potassic cyanide; soluble, however, in aqua regia and in potassic or sodic sulphide in the presence of sodic hydrate, but insoluble in their sulphydrates. Long digestion with concentrated nitric acid converts the black HgS into a white body, consisting of $2HgS + Hg(NO_3)_2$.

SAm_2 gives the same precipitate.

$NaHO$ or KHO added in excess produces a *yellow* precipitate of **mercuric oxide**, HgO, insoluble in excess.

$AmHO$ produces a *white* precipitate of **mercuric ammonic chloride**, $2(NH_2Hg''Cl)$, known as "*white precipitate.*"

Sodic or potassic carbonates give a *reddish-brown* basic precipitate.

KI gives a *bright red* precipitate of **mercuric iodide**, HgI_2, soluble either in excess of potassic iodide or of the mercuric salt.

KCy gives with mercuric nitrate (not the chloride) a *white* precipitate of **mercuric cyanide**, $HgCy_2$, soluble in excess; not decomposed by boiling with alkalies or alkaline carbonates, but only by SH_2.

Mercuric salts are readily reduced to mercurous salts:—

$SnCl_2$ (**stannous chloride**) gives with mercuric salts a *white* precipitate of **mercurous chloride**, Hg_2Cl_2, which when boiled with excess of the reagent, is reduced to grey metallic mercury. On pouring off the solution and boiling the grey precipitate with HCl, the mercury is obtained in little globules.

$FeSO_4$ (**ferrous sulphate**) reduces $\substack{NO_3\\NO_3}Hg$, but not $HgCl_2$, to the metallic state.

Cu, Zn, Fe, precipitate metallic mercury from mercuric solutions, provided they are not too acid.

If a strip of bright metallic copper be employed, a silvery-white deposit of metallic Hg is obtained, which, when gently rubbed, shows a bright metallic lustre, and gives, after drying and heating in a dry and narrow test-tube, a sublimate of *metallic* mercury.

Mercuric salts act the part of *oxidizing agents;* they are first reduced to mercurous salts, and finally to metallic mercury.

QUESTIONS AND EXERCISES.

1. What changes take place when the sulphides of As, Sb, and Sn are boiled, 1st, with SAm_2, 2nd with NaHO? Express the changes by equations?
2. Give the graphic formulæ of cinnabar, dimercuric sulpho-dichloride, of *white precipitate* and of mercuric nitrate.
3. Write out the symbolic equations for the reactions which mercuric nitrate gives with the group and special reagents.
4. Calculate the percentage composition of *white precipitate.*
5. How is *corrosive sublimate* manufactured, and whence does it derive its name?
6. 1·5 grm. of $HgCl_2$ is precipitated as HgS and collected on a weighed filter. How much by weight of HgS should there be obtained?
7. *Cinnabar* is sometimes found adulterated with red-lead, red oxide of iron, brick-dust. State how you would discover the adulteration. (No separation of the impurities from each other is required.)
8. What reaction takes place when mercury is acted upon by a concentrated sulphuric acid? and by what consecutive stages is the product of this reaction converted into *white precipitate?*

2. **LEAD,** Pb'' and ^{vi}.—Only a slight precipitate of PbS is for the most part obtained in Group II, since the greater part of the lead is removed in Group I as $PbCl_2$. It happens frequently that this small quantity of lead is not precipitated by SH_2, on account of the solution being too acid (HCl), or too concentrated, in which case a little lead is found in Group III, and is often mistaken for some other metal. It is necessary, therefore, to dilute a portion of the filtrate from Group II considerably and to pass a current of SH_2 through, in order to make sure of the presence of lead, especially so, when lead has been discovered in Group I; and, if a precipitate be obtained, to pass the gas once more through the whole of the filtrate, after having diluted it considerably with distilled water.

3. **BISMUTH,** Bi''' and ^{v}.—This metal is principally found native; also in combination with oxygen and sulphur, as *bismuth ochre,* Bi_2O_3, from the decomposition of *bismuth glance,* Bi_2S_3, and in the form of sulpho-salts, as *kobellite,* $Bi_2S_3(PbS)_3$ (trisulphoplum

bic orthosulpho bismuthite), and as *needle ore*, $Bi_2S_2(PbS)_2(Cu_2S_2)$, disulphoplumbo-cuprous orthosulpho-bismuthite.

EXAMINATION IN THE DRY WAY.

The metal is highly crystalline and of a slightly red colour. It has an atomic weight of 207·52, and specific gravity 9·80, and fuses at 266·8° C., and boils between 1090° and 1450° C. Air has only a very slight effect on the metal at ordinary temperatures, but oxidizes it rapidly when heated above its melting point. Nitric acid is the only acid which acts readily upon it. It expands on solidifying from fusion. It is not volatile excepting at a very high temperature.

The metal bismuth fuses with ease, both in the reducing and oxidizing flame of the blowpipe, covering the charcoal with an incrustation of oxide, **orange-yellow**, *while hot*, **lemon-yellow**, *when cold*, passing at the edges into a **bluish-white**. The incrustation can be driven from place to place by either flame, *without colouring* the outer flame. (Distinction from Lead.) Heated with borax or microcosmic salt, Bi_2O_3 gives beads which are *yellowish*, when hot, and *colourless*, when cold. All bismuth compounds can be reduced to the metallic state by heating on charcoal with sodic carbonate in the inner or reducing flame. The metallic bead is brittle. (Distinction from Lead and Silver Beads.)

EXAMINATION IN THE WET WAY.

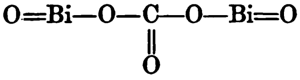
Bismuth dissolves readily in nitric acid, forming $Bi(NO_3)_3$. A solution of this salt is conveniently employed.

SH_2 (**group-reagent**) gives a *brownish-black* precipitate of **bismuthous sulphide**, Bi_2S_3, insoluble in dilute acids, in alkalies and in alkaline sulphides; soluble in concentrated nitric acid.

Alkaline sulphides give the same precipitate.

KHO, NaHO and AmHO produce a *white* precipitate of **bismuthous hydrate**, $BiHO_3$, insoluble in excess.

Alkaline carbonates throw down a *white bulky* precipitate of **basic carbonate** (*bismuthylic carbonate*) $BiCO_3BiO_2 = CO(BiO_2)'_2$, graphic formula:—



$$O{=}Bi{-}O{-}\underset{\underset{O}{\|}}{C}{-}O{-}Bi{=}O$$

in which the compound radical **bismuthyl**, BiO, acts the part of H in HO. The precipitate is insoluble in excess.

$Cr_2O_5(KO)_2$ gives a *yellow* precipitate of **basic chromate** = $\left\{\begin{array}{l}CrO_2(BiO_2)'\\ O\\ CrO_2(BiO_2)'\end{array}\right.$ readily soluble in dilute nitric acid, insoluble in potassic hydrate. (Distinction from Plumbic Chromate.

H_2SO_4 gives no precipitate. (Distinction from Lead.)

KI produces a *brown* precipitate of **bismuthous iodide**, BiI_3, soluble in excess.

KCy produces a *white* precipitate, insoluble in excess, soluble in acids.

Bismuthous salts are partially decomposed by *water*, a basic salt being precipitated. The addition of an acid redissolves the precipitate. This constitutes the most characteristic reaction for bismuthous salts. The salt most readily precipitated is the chloride ($BiCl_3$). It can be prepared from the nitrate by precipitating the oxide first, and then filtering and dissolving the precipitate off the filter with dilute hydrochloric acid. Excess of acid should be avoided.

OH_2 gives with $BiCl_3$ a *white* precipitate of **bismuthous oxychloride**, BiOCl, which is almost absolutely insoluble in water, but soluble in hydrochloric acid, from which it is reprecipitated on the addition of ammonic or sodic chloride. BiOCl is insoluble in tartaric acid. (DISTINCTION FROM ANTIMONY.)

Metallic zinc precipitates bismuth from its salts.

Bismuthous salts exhibit a tendency to form basic salts, showing that Bi_2O_3 is a very indifferent and weak base.

There are several oxides known, *e.g.*, **bismuthic oxide** or **anhydride**, Bi_2O_5, which parts readily with two atoms of oxygen, when heated or acted upon by reducing agents; Bi_3O_7 and others.

QUESTIONS AND EXERCISES.

1. How can Bi be separated from Ag, Pb, or Hg?
2. Express in symbolic equations the reactions which a bismuthous salt gives with different reagents in the wet way.
3. Give the graphic formulæ for bismuthous nitrate, bismuthous oxide, *bismuth glance*, bismuthous oxychloride.
4. Calculate the percentage composition of an alloy of 1 atom of Pb, 1 atom of Sn, and 3 atoms of Bi.

4. **COPPER**, Cu''.—This metal is found native; also in combination with OXYGEN and SULPHUR, as *red copper ore* or *ruby ore*, Cu_2O, as *vitreous copper* or *copper glance*, Cu_2S, and *indigo copper* or *blue copper*, CuS; more frequently as *copper pyrites*, Fe_2S_3,Cu_2S $= \left\{\begin{matrix} FeS \\ FeS \end{matrix}\right.(Cu_2S_2)''$, (diferric cuprous tetrasulphide), and *variegated copper* or *horseflesh ore*, $Fe_2S_3,3Cu_2S$, also as *fahl ore*, *bournonite*, etc.; in combination with CARBONIC ACID, as basic carbonate, *malachite*, $CO(OCuHO)_2$, and *azurite*, *mountain blue*, or *copper azure*, $\begin{matrix} CHOCuO_2 \\ CHOCuO_2 \end{matrix} CuO_2 = C_2Cu_3O_8H_2$; with SULPHURIC ACID, as *blue vitriol* = $CuSO_4 5OH_2$, with PHOSPHORIC ACID, as *phosphorocalcite*, *libethenite*; with ARSENIOUS ACID, as *tennantite*, SILICIC ACID, as *dioptase*, and others.

Copper is extracted from its sulphides by a combination of oxidizing and reducing processes. It is the only metal of a decided red colour. Its atomic weight = 63·17. Specific gravity = 8·92, and melts at 1054° C.

On exposure to air, it oxidizes at ordinary temperatures, and rapidly when heated to redness. Water has no action on copper at any temperature, but most acids attack it especially if exposed to the air at the same time. Alkalies, including lime and ammonia, also act upon it. Liquefied NH_3 dissolves it. It is one of the best conductors of heat and electricity.

EXAMINATION IN THE DRY WAY.

Copper minerals form a very numerous class of ores; and as many of them exhibit precisely similar blowpipe reactions, a knowledge of their physical character is indispensable to enable the student to distinguish readily between them. It is advisable to examine the doubtful ores in the wet way also.

The most characteristic reaction in the dry way is that which copper compounds give, when heated in a bead of borax or microcosmic salt before the blowpipe flame. The bead is **green** *whilst hot*, **blue** *on cooling*. Most copper compounds, when heated on platinum wire in the inner flame, impart an **intense green** colour to the outer flame. All copper compounds are reduced when heated in the inner flame on charcoal, together with sodium carbonate and potassium cyanide, yielding red metallic scales, or globules. Sulphides give off SO_2, when roasted in an open tube, and leave CuO behind. *Malachite* or *azurite* gives off water and carbonic anhydride when gently heated in a tube. Blue vitriol loses water, sulphurous anhydride and oxygen, and leaves cupric oxide. Cupric phosphate, arsenate, and silicate fuse to coloured glasses.

Metallic copper is not affected in dry air at the ordinary temperature, but is readily oxidized when heated in air or oxygen and converted into black cupric oxide. Hydrochloric acid in the presence of air dissolves copper slightly, forming Cu_2Cl_2; nitric acid is the most active solvent for copper (as it is for Ag, Hg, Pb, and Bi), forming cupric nitrate. Sulphuric acid (concentrated) dissolves copper, on heating, with evolution of SO_2, and formation of $CuSO_4$.

$SO_2(HO)_2$ acts here the part of an oxidizing agent. This method of preparing sulphurous anhydride gas is frequently employed in the laboratory in preference to other methods.

EXAMINATION IN THE WET WAY.

A SOLUTION OF CUPRIC SULPHATE, $CuSO_4$, OR CUPRIC NITRATE, $\genfrac{}{}{0pt}{}{NO_2}{NO_2}CuO_2$, may conveniently be employed.

SH_2 (**group reagent**) gives a *brownish-black* precipitate of **cupric sulphide**, CuS, insoluble in dilute acids: slightly soluble in yellow ammonic sulphide; soluble with decomposition in nitric acid; completely soluble in potassic cyanide; insoluble in potassic and sodic sulphides or caustic alkalies. CuS is rapidly oxidized to $CuSO_4$ by exposure to the air; it is insoluble in hot dilute sulphuric acid.

SAm_2 produces the same precipitate, somewhat soluble in excess, especially in yellow ammonic sulphide.

NaHO or KHO gives a *light-blue* precipitate of **cupric hydrate**, $Cu(HO)_2$. The precipitate turns black on boiling and becomes denser. Three molecules of $Cu(HO)_2$ lose two molecules of OH_2 and leave $3CuO,OH_2$(graphic formula H—O—Cu—O—Cu—O—Cu—O—H). In the presence of many organic substances, such as grape sugar, etc., the precipitate dissolves to a deep blue solution, whence the whole of the copper is reprecipitated on boiling in the form of *bright red* **cuprous oxide**, Cu_2O.

Sodic, or potassic carbonate produces a *greenish-blue* **basic carbonate**, of the composition $CO(OCu''HO)'_2$, (graphic formula) $O = C\begin{smallmatrix}\diagup O—Cu—O—H \\ \diagdown O—Cu—O—H\end{smallmatrix}$, carbonic anhydride being evolved. This precipitate is converted on boiling into the black precipitate of $3CuO,OH_2$. It is soluble in ammonic hydrate to an azure-blue, and in potassic cyanide to a colourless fluid forming a soluble double cyanide.

AmHO or Am_2CO_3, when added in small quantities, produces a *greenish-blue* precipitate of a **basic salt**, which dissolves readily in excess of the reagents, and forms a magnificent *azure-blue* liquid,—a blue which is perceptible, if a solution contain small traces of copper only. The blue solution contains a double compound of **cuprammonic hydrate**, $N^v{}_2H_6Cu''(HO)_2$, and **ammonic sulphate**, or ammonio cupric sulphate, $SO_4\begin{pmatrix}NH_3.NH_3 \\ NH_3.NH_3\end{pmatrix}Cu,OH_2$ or, $SO_2\begin{smallmatrix}NH_3HO \\ NH_3HO\end{smallmatrix}\left(\begin{smallmatrix}NH_3 \\ NH_3\end{smallmatrix}CuO\right)$, whence the black cupric oxide separates on boiling with sodic hydrate.

This tendency of ammonia to combine with cupric hydrate and to form cuprammonic hydrate induces metallic copper to combine with oxygen even at the *ordinary temperature* when in contact with ammonia.

KCy gives a *greenish-yellow* precipitate of **cupric cyanide**, $CuCy_2$, soluble in excess. SH_2 produces *no precipitate* from this solution.

K_4FeCy_6 gives a *reddish-brown* precipitate of **cupric ferrocyanide**, Cu_2FeCy_6, insoluble in dilute acids, decomposed by potassic or sodic hydrate, with separation of $3CuO,OH_2$. Even in very dilute solutions of copper salts a brownish colour is produced,—best seen when the reaction is performed on a watch glass, placed on a sheet of white paper or in a little porcelain dish. Hence K_4FeCy_6 supplies one of the most delicate reactions for copper salts.

Metallic zinc or iron precipitates metallic copper, especially in the presence of a little free hydrochloric acid. If a few drops of a slightly acidulated dilute copper solution are placed on platinum foil (the lid of a platinum crucible), together with a small piece of sheet zinc, the platinum becomes rapidly coated with a reddish film of metallic copper, visible even in the case of very dilute solutions, an equivalent quantity of the metal zinc being dissolved.

This simple experiment requires some explanation. Bright copper is not attacked by dilute hydrochloric or sulphuric acid.